STUDIES ON
TRIPHENYLPHOSPHINE AND TRIPHENYLARSINE COMPLEXES
OF RUTHENIUM (III) AND RUTHENIUM (II)

A Thesis Submitted
in partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
K. NATARAJAN

to the

DEPARTMENT OF CHEMISTRY
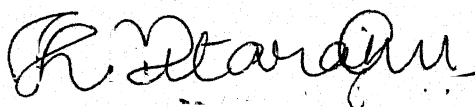INDIAN INSTITUTE OF TECHNOLOGY KANPUR.
JULY, 1976

TO

AMMA, APPA AND MAMA

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of the investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervision of Professor U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.
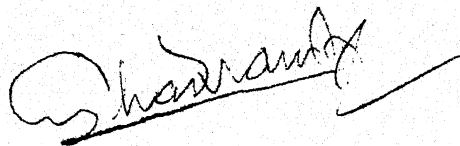
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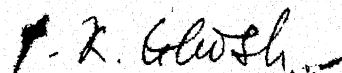
CERTIFICATE OF COURSE WORK

This is to certify that Mr. K. Natarajan has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 500	Mathematics for Chemists
Chm 501	Advanced Organic Chemistry I
Chm 521	Chemical Binding
Chm 523	Chemical Thermodynamics
Chm 524	Modern Physical Methods in Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 542	Advanced Inorganic Chemistry II
Chm 634	Symmetry and Molecular Structure
Phy 656	X-ray Diffraction and Crystal Structure
Chm 800	General Seminarr
Chm 801	Graduate Seminar
Chm 900	Post-Graduate Research

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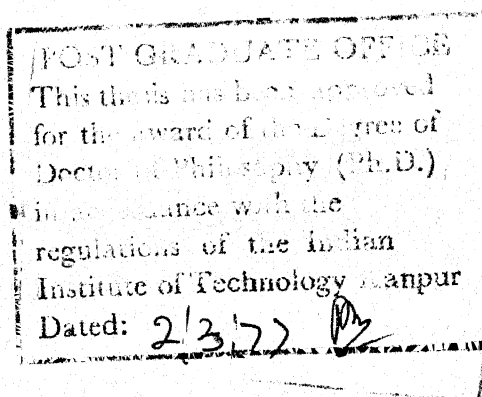Department of Chemistry
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Certified that the work contained in this thesis, entitled "STUDIES ON TRIPHENYLPHOSPHINE AND TRIPHENYL-ARSINE COMPLEXES OF RUTHENIUM(III) AND RUTHENIUM(II)" has been carried out by Mr. K. Natarajan under my supervision and the same has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENT

PREFACE

Tertiary-phosphines and arsines form complexes with transition metals which are of importance because of their interesting molecular structure, physical and chemical behaviours. The complexes of ruthenium are of special interest because they act as good catalysts in many reactions and serve as starting materials for the syntheses of new complexes. Present work deals with the reactions of some of the ruthenium(III) and ruthenium(II) complexes of tertiary-phosphine and arsine with various ligands and their various physical and chemical properties needed for the understanding of their structures.

Chapter I describes the scope of the work and a brief literature survey regarding the nature of Metal-Phosphorus and Metal-Arsenic bond. The work done on ruthenium(II) and ruthenium(III) tertiary-phosphine and arsine complexes in the recent years has also been described in this chapter.

In Chapter II, a detailed investigation of the reactions of $[RuCl_3(AsPh_3)_3]$ with ligands containing nitrogen, sulphur and oxygen donor atoms has been presented and the physical and chemical properties of the resulting compounds discussed.

Chapter III describes some further reactions carried out on $[RuCl_3(AsPh_3)_3]$ together with the preparation of a new

ruthenium(III) complex [RuBr$_3$(AsPh$_3$)$_3$]. The results of the physicochemical methods used to understand their structures have been discussed.

Chapter IV deals with the reactions carried out on some ruthenium(III) triphenylphsphine and triphenylarsine complexes with β -diketones. The physical and chemical properties of the compounds obtained have been studied with various physico-chemical techniques and their structures have been proposed.

In Chapter V, a thorough reinvestigation of the compound [RuCl$_3$(AsPh$_3$)$_2$(OAsPh$_3$)]has been presented alongwith the preparations of some new ruthenium(II) and ruthenium(III) complexes. Their structures have been postulated on the basis of the studies carried out on these complexes.

Chapter VI describes some of the reactions of β-diketones with ruthenium(II) hydrido-carbonylphosphine complexes and the results of the studies carried out on the products.

CONTENTS

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SCOPE AND OBJECTIVE OF THE WORK

Complexes of transition metals with tertiary-phosphines
and arsines have gained considerable interest during the last
two decades.[1-3] Attempts have been made to understand the nature
of bond formed between the metal ion and the phosphorus or arsenic
atom of the ligand in such complexes. Plenty of information is
available regarding the nature of metal-phosphorus bond for phos-
phorus containing ligands. However, the nature of bond formed
between metal and heavier Group VB donor elements is not still
well established.[3]

A very large number of complexes of ruthenium(III) and
ruthenium(II) with tertiary-phosphines have been synthesized
and studied in detail, but not much literature is available on
the complexes of ruthenium(II) and especially of ruthenium(III)
with tertiary mono-arsines. Most of the ruthenium(II) and a few
of the ruthenium(III) complexes containing tertiary-phosphines

and arsines have been used as catalysts[4-16] in many reactions, e.g., hydrogenation, oxidation, hydroformylation, hydration, polymerisation, carbonylation, decarbonylation, dehydrogenation, desulphonylation, isomerisation and alkylation and some of the complexes have been used as starting materials[17-74] for the syntheses of novel ruthenium(II) and ruthenium(III) complexes containing tertiary phosphines and arsines bonded to metal ion besides other ligands. It will, therefore, be interesting to study the reactions of ruthenium(III) and ruthenium(II) complexes of tertiary-phosphines and arsines with various ligands leading to the formation of new complexes and to investigate their structures. The possibility of using them as catalysts in various reactions and as starting materials for the syntheses of new compounds will also be interesting to study.

In this thesis, the reactions of $[RuCl_3(AsPh_3)_3]^-$ with various ligands containing nitrogen, oxygen and sulphur donor atoms have been discussed and the structures of the complexes, thus formed have been postulated by studying their ir, visible, magnetic and other physical studies. The compounds obtained are of the type (i) $[RuCl_3(AsPh_3)_2L]$ ($L = CH_3CH_2CH_2CN$, $CH_2=CHCN$, dmf, CH_3CHO, C_6H_5CHO etc.), (ii) $[RuCl_3(AsPh_3)L]$ ($L = $ bipy, 1,10 phen, $(Me_2S)_2$), (iii) $[RuCl_2(AsPh_3)_2L_2]$ ($L = CH_3CN$, $CH_3CH_2CH_2CN$, $CH_2=CHCN$) and (iv) $Me_4N[RuCl_3X(AsPh_3)_2]$ ($X = Br$ or I). On the basis of the study of the electronic spectra of the complexes an equilibrium between hexa- and penta-coordinated species in

solution has been postulated.

Further reactions of $[RuCl_3(AsPh_3)_3]$ with K/Na thiocyanate, carboxylates, ammonia, amine and hydrazines have also been studied. The reactions of the complex with thiocyanates and carboxylates gave $[Ru(SCN)_3(AsPh_3)_2]$ and $[RuCl_2(AsPh_3)_2(RCOO)](R = CH_3, C_2H_5)$ respectively, while those with ammonia, amine and hydrazines gave ruthenium(II) complexes of the type $[RuCl_2(AsPh_3)_2L_2]$ ($L = NH_3$, CH_3NH_2, NH_2NH_2, $C_6H_5NHNH_2$). Besides this, a new ruthenium(III) complex $[RuBr_3(AsPh_3)_3]$ has also been synthesized.

The reactions of β-diketones with some of the ruthenium-(III) phosphine and arsine complexes, viz., $[RuX_3(EPh_3)_3]$ ($X = Cl$, Br; $E = P$, As) and $[RuBr_3(PPh_3)_2.MeOH]$ gave compounds of the type $[RuX_2(bdk)(EPh_3)_2]$ (bdk = acetylacetonate, dibenzoylmethanate, benzoylacetonate; $E = P$, As; $X = Cl$, Br). Most of these complexes showed higher magnetic moment values which have been explained assuming a thermal equilibrium between spin paired and spin free states. The esr study of these complexes have also been done. The reactions of β-diketones with ruthenium(II) hydrido carbonyl complexes, viz., $[RuH_2(CO)(PPh_3)_3]$ and $[RuHCl(CO)(PPh_3)_3]$ have been studied and the products characterised. Moreover, β-diketones reacted with $[RuCl_2(PPh_3)_2]_n$ and $[RuCl_2(AsPh_3)_2]_2$ to give dimeric ruthenium(II) complexes of the type $RuCl(bdk)(EPh_3)_{2\,2}$.

Finally, reinvestigation on the ruthenium(III) complex $[RuCl_3(AsPh_3)(OAsPh_3)_2]$ revealed that it should have been formulated as $[RuCl_3(AsPh_3)_2(OAsPh_3)]$. Two new complexes

[$RuCl_3(NO)(AsPh_3)(OAsPh_3)$] and [$RuCl_2(CO)_2(AsPh_3)(OAsPh_3)$] have been prepared from the reactions of [$RuCl_3(AsPh_3)_2(OAsPh_3)$] and NO and CO gases. A new isomer of [$RuCl_3(AsPh_3)_3$] has been synthesized from [$RuCl_3(AsPh_3)_2 \cdot MeOH$] with excess of triphenylarsine. On the basis of the esr spectra of the brown and pink compounds, it has been shown that the former compound should have C_{3v} symmetry and the latter, C_{2v} symmetry.

PRESENT STATUS OF METAL-PHOSPHORUS BOND

In the middle of this century a kind of similarity was noted between carbon monoxide, phosphorus and arsenic donors in their ability to form complexes with transition metals. Based on Pauling's theory of metal carbonyl double bonding, J. Chatt[75] surmised that phosphorus, in ligands such as tertiary phosphines had vacant d-orbitals capable of accepting electrons from filled metal d-orbitals and thus, forming a "dative π-bond" in addition to the ligand-metal σ-bond. The transfer of electron density from the metal to ligand would be promoted by electronegative groups bonded to phosphorus. Chatt[75] tested the theory by studying the interaction of phosphorus trifluoride with platinum(II) chloride and boron trifluoride where platinum formed stuitable complexes and boron, which has no electrons available for dative π-bond formation did not have any significant interaction with phosphorus trifluoride. This suggestion of back bonding or

$d_\pi - d_\pi$ overlap between the metal and donor atoms was also introduced by Nyholm and coworkers.[76,77] Much of the discussion about the nature of bond between phosphorus and metals has centered on the relative importance of σ or π contributions to the metal-ligand bonding and this topic remains one of considerable controversy.

Regarding the nature of bonding between metal ion to phosphorus containing ligands it appears to be reasonably clear that the metals in oxidation state (II) or higher form pure σ-bonds with alkyl or aryl phosphines. In complexes in which the metal is in zero or (-I) oxidation state there is an extensive participation of σ- and π-bond. For intermediate situations due to either lack of suitable results or lack of agreement concerning their interpretation, there is uncertainty in the degree of π-character in the M-P bond. These conclusions are based on the results of the studies carried out using various physical methods[78-96] (Table I.1).

For bonds between metal to ligands containing heavier group VB atoms, there are no systematic studies and therefore, the results are few in number. However, it appears that the arsines as ligands behave very similar to the phosphines and therefore, it may be that the tertiary arsines also form σ - bonds with higher oxidation states of metal. This assumption may not be correct as was pointed out by Pauling[97] who noted that Co-As and Mn-As bonds in trans-$[CoCl_2(diarsine)_2]^+$ and

Table I.1

The studies on M-P bond

Complex	Physical methods used	Inference	Reference
$[PtX_2(PR_3)_2]$	^{31}P nmr	σ -bond	79
cis- and trans- $[PtCl_2(PR_3)_2]$	Bond energy measurement	σ - and π -bond	80
trans-$[PtMe(CO)(AsMe_3)_2]^+$	^{13}C nmr	σ -bond	81
trans-$[PtXY(PR_3)_2]$ (X = anionic ligand; Y = m-fluorophenyl)	^{19}F nmr	σ -bond	82
trans-$[PtXY(PR_3)_2]$ (Y = p-fluorophenyl)	^{19}F nmr	σ + π-bond	82
$[W(CO)_5L]$ (L = PR_3)	ir	σ + π -bond	83,84
Ni(O) complexes of di-arsine and diphosphine	Bond order measurement	σ + π -bond	85
cis- and trans- $[PtCl_2(PR_3)_2]$ $[PdCl_2(PR_3)_2]$ and $[M(PR_3)_2(CO)_4]$ (M = Cr, Mo, W)	^{31}P nmr	σ + π -bond	86-93
$[Ni(CO)_2(PR_3)_2]$	^{31}P nmr	σ + π -bond	94,95
Trifluorophosphine complexes of Ni	ir, nmr, dipole moment	strong π -bond	96

$[\{Mn(\pi -MeC_5H_4) (CO)_2\}_2(diarsine)]$ are shorter than their respective estimated single bond distances. But similar shortening of the M-P bond length has also been observed for metals in quite high oxidation states. It has been suggested that the metal radii are quite significantly dependent on the nature of ligands.[98]

Various physical studies on the Pt(II), Fe(II) and Fe(III) complexes with arsenic and antimony donors indicate the $\sigma + \pi$ interaction increases in the order $Ph_3As < Ph_3Sb < Ph_3P$ and the study of pentacyanato Fe(II) and Fe(III) derivatives suggested that π-affinity of Ph_3As and Ph_3Sb are similar and lower than that of Ph_3P.[99,100]

TERTIARY-PHOSPHINE AND ARSINE COMPLEXES OF RUTHENIUM(II)

There has been a considerable and growing interest in the chemistry of ruthenium(II) complexes with mono-tertiary phosphine, arsine and stibine. Many hydride, carbonyl and hydrido carbonyl complexes of ruthenium(II) with tertiary-phosphine and arsine have also been reported.[3]

Some of the ruthenium(II) complexes have been used as catalysts for a variety of reactions, including hydrogenation, oxidation, hydroformylation, hydration, polymerisation, carbonylation, decarbonylation, dehydrogenation, desulphonylation, isomerisation and alkylation. A review article by B.R. James[4] describes these

reactions covering literature till 1969. Some important ruthenium(II) complexes showing these properties are $[RuCl_2(PPh_3)_3]$, $[RuCl_2(PPh_3)_4]$, $[RuHCl(PPh_3)_3]$ and $[RuH(OCOCH_3)(PPh_3)_3]$.

$[RuCl_2(PPh_3)_3]$ has been found to have a distorted square pyramidal structure[17] having trans-chlorine atoms and trans-phosphorus atoms in the base and an apical phosphorus atom. Ruthenium atom lies close to the centre of the square pyramid. Apical Ru-P distance is shorter by 0.16 Å than the basal Ru-P distance. The unused octahedral site is blocked by a phenyl ring. Some interesting reactions of $[RuCl_2(PPh_3)_3]$ are given in Table I.2.

An active and much studied catalyst for hydrogenation is $[RuHCl(PPh_3)_3]$. It is prepared[18] from $[RuCl_2(PPh_3)_3]$ and sodium borohydride in benzene solution containing little water. It is found to have a distorted trigonal bipyramidal geometry,[20] where the two axial triphenylphosphine groups bend from the perpendicular position to accommodate the equatorial phenyl groups. The chlorine atom occupies the second equatorial position, but the hydride hydrogen can not occupy the expected position in the equatorial plane because of the proximity of a phenyl α-hydrogen almost in the plane at 2.85 Å from the ruthenium atom. The hydride hydrogen is displaced such that the equatorial P-Ru-H angle is approximately 89°.

Many carbonyl phosphine and arsine complexes of ruthenium-(II) are reported to have been prepared from the carbonyls or

Table I.2

Reactions of $RuX_2(PPh_3)_n$ (n = 3 or 4)

Reaction	Compound obtained	Physical properties	Ref.
1	2	3	4
$RuCl_2(PPh_3)_3$ + H_2 + $NaBH_4$ + benzene	$RuHCl(PPh_3)_3$	X, IR, NMR	18, 20
$RuCl_2(PPh_3)_3$ + H_2 + $(C_2H_5)_3N$	$RuH_2(PPh_3)_3$	IR	21
$RuCl_2(PPh_3)_3$ + CS_2	a) $[RuCl_2(CS)(PPh_3)_2]_2$ b) $[RuCl(CS_2)(PPh_3)_3]Cl$	IR	22
$RuCl_2(PPh_3)_3$ + L (L=RCN, amine)	$RuCl_2(PPh_3)_2L_2$	IR	23
$RuCl_2(PPh_3)_3$ + L (L=β-diketonate, carboxylate)	cis- and trans- $Ru(PPh_3)_2L_2$	IR	23
$RuCl_2(PPh_3)_3$ + L (L=$R_2NCS_2^-$, $ROCS_2^-$ where R=Me, Et, Ph)	$Ru(PPh_3)_2L_2$	IR	24
$RuCl_2(PPh_3)_3$ + $ROCO^-$ + H_2 (R=Me, Et, Ph, Pr^n, Pr^i, CF_3, CMe_3)	$RuH(OCOR)(PPh_3)_3$	X, IR, NMR	19, 25
$RuCl_2(PPh_3)_3$ + $C_2H_5COCH_3$	$[Ru(PPh_3)_2Cl_2]_2$	IR	23

Table I.2 (contd.)

1	2	3	4
$RuX_2(MPh_3)_3$ + CNEt (X=Cl, Br; M=P, Sb)	$RuX_2(MPh_3)_2(CNEt)_2$	IR	26
$RuCl_2(PPh_3)_3$ + $P(OR)_3$ (R=Ph, p-C_6H_4Cl, p-C_6H_4Me, C_2H_4Cl)	$RuCl_2 P(OR)_3$ 4	IR, NMR	27
$RuX_2(PPh_3)_4$ + C_7H_8 (X = Cl, Br; C_7H_8 = bicyclo(2.2.1)hepta-2,5-diene)	$RuX_2(PPh_3)_2(C_7H_8)$	IR	28
$RuX_2(PPh_3)_4$ + CO (X = Cl, Br)	trans-[$RuX_2(CO)_2(PPh_3)_2$]	IR	29

X = X-ray structural determination,

IR = infrared

NMR = nuclear magnetic resonance.

the phosphino carbonyls of ruthenium. Complexes of the type $[RuX_2(CO)_2L_2]^{30-42}$ (L = PPh_3, $AsPh_3$, PEt_3, $AsEt_3$, PEt_2Ph, $PEtPh_2$, $PMePh_2$, $P(C_6H_{11})_3$, $AsMePh_2$, $PhCH_2PMe_2$, $PhCH_2AsMe_2$ and X = Cl, I; L = PPh_3, PEt_3 and X = H), $[RuX_2(CO)_3(PPh_3)]^{42-44}$ (X = Cl, Br, I) and $[RuX_2(CO)_2(PPh_3)]_2{}^{44}$ (X = Cl, Br, I) were prepared using various carbonyls e.g., $[Ru(CO)_2X_2]_n$ (X = Cl, I), $[Ru_3(CO)_{12}]$, $[Ru(CO)_3(PR_3)_2]$ and $[Ru_3(CO)_9(PR_3)_3]$.

A dinitrogen complex of ruthenium(II) viz., $[Ru(N_2)(PPh_3)_3H_2]$ was obtained by Yamamoto et al.[45,46] in solution, whereas Knoth[47] isolated and characterised it. This complex looses nitrogen when treated with triphenylphosphine, ammonia, hydrogen and hydrogen chloride gas to give $[RuH_2(PPh_3)_4]$, $[RuH_2(NH_3)(PPh_3)_3]$, $[RuH_4(PPh_3)_3]$ and $[RuCl_2(PPh_3)_3]$ respectively.

Some ruthenium complexes with dioxygen of the type $[RuX(NO)(PPh_3)_2(O_2)]^{48-51}$ (X = Cl or NCS) are also reported. They act as catalyst in the oxidation of triphenylphosphine to triphenylphosphine oxide by molecular oxygen. Graham et al.[50,51] have studied the kinetics of oxidation of triphenylphosphine in the presence of $[Ru(NCS)(NO)(PPh_3)_2(O_2)]$ and have postulated a mechanism for the oxidation.

TERTIARY-PHOSPHINE AND ARSINE COMPLEXES OF RUTHENIUM(III)

Eventhough there has been extensive research carried out on ruthenium(II) tertiary phosphine and arsine complexes, the

study on ruthenium(III) is relatively less. However, the study
regarding the complexes of ruthenium(III) with tertiary arsines
seems to be a neglected one. Ruthenium(III) tertiary-phosphine
and arsine complexes described in the literature are discussed
here in this section.

Nyholm et al.[101] reported the preparations of ruthenium(III)
complexes with O-phenylenebis-dimethylarsine (DA). The complexes
they have obtained are $[RuX_2(DA)_2][RuX_4(DA)]$ (X = Cl, Br) and
$[RuX_2(DA)_2]Y$ (X = Cl, Y = Cl; X = Br, Y = Br; X = Cl, Y = ClO_4; X = I,
Y = ClO_4). These complexes were prepared by the oxidation of the
ruthenium(II) complexes $[RuX_2(DA)_2]$ (X = Cl, Br) by chlorine and
bromine.

The only known ruthenium(III) carbonyl phosphine complex
$[RuBr_3(CO)(PPh_3)_2]$ has been prepared by Vaska[102] along with other
ruthenium(III) complexes $[RuX_3L_2.MeOH]$ (X = Cl, Br; L = PPh_3,
AsPh_3). The preparation, magnetic and dipolemoment studies have
been reported for $[RuCl_3(MEt_2Ph)_3]$[103] (M = P, As). Stephenson
et al.[104] reported complexes of the type $[RuX_3L_2MeOH]$ (X = Cl, Br;
L = PPh_3, AsPh_3 and $M[RuCl_4L_2]$ (M=Et_2PhPH, Et_3PH; L = PEt_2Ph, PEt_3).
Nicholson[105] reported the preparation of mixed ruthenium(II) and
ruthenium(III) complexes $[Ru_2Cl_5L_4]$ and a dimeric ruthenium(III)
complex $[RuCl_3L_2]_2$ (L = PPr_3^n, PBu_3^n). The dimeric complex
$[RuCl_3L_2]_2$ has been formulated as halogen bridged dimer. The
complex $[Ru_2Cl_5(PBu_3^n)_4]$ has been shown by X-ray structure[106]
analysis to be analogous to the $[Ru_2Cl_3(PR_3)_6]Cl$ complexes

(postulated to contain a triple chloride bridge)[107] with two chloride ions replacing two phosphine groups to give a neutral complex with formal mixed oxidation states of ruthenium(II) and ruthenium(III).

Various methods of the preparation of the complexes mer-$[RuX_3L_3]$ (X = Cl, Br; L = PMe_2Ph, PEt_2Ph and X = Cl, L = PBu_2^nPh, PPh_3) have been reported, culminating in a paper by Chatt et al.[108] in which a general preparative method has been given. Further papers have discussed the esr[109] and configuration[110] of these and other platinum-metal tertiary phosphine and arsine complexes. $[RuCl_3(PPr_2^nPh)_3]$[111] has been prepared by the reaction of $RuCl_3.3H_2O$ and PPr_2^nPh. Recently the preparations of $[RuCl_3(AsPh_3)_3]$ and $[RuCl_3(AsPh_3)(OAsPh_3)_2]$ have been reported along with some of their reactions.[112]

Some of the reactions carried out on ruthenium(III) tertiary phosphine and arsine complexes are given in Table I.3.

Much of the reactions of ruthenium(III) tertiary phosphine and arsine complexes have come from Stephenson et al.[113,114] Reactions of tetramethylammonium and tetraphenylarsonium halides with complexes $[RuX_3L_2MeOH]$ (X = Cl, Br; L = PPh_3, $AsPh_3$) gave ionic complexes of the type $M[RuX_4L_2]$ (M = Ph_4As^+, Me_4N^+; L = PPh_3, $AsPh_3$; X = Cl, Br) and $M[RuCl_4(PR_3)_2]$ (M = Ph_4As^+, Me_4N^+; PR_3 = PEt_3, PPh_3, PMe_2Ph). He has also obtained $[RuCl_3(AsPh_3)_2(CH_3NO_2)]$,[113] $[RuBr_3(PPh_3)_2H_2O]H_2O$[114] and $H[RuCl_4(PPh_3)_2]$.[114]

Table I.3

Reactions of some ruthenium(III) complexes with various ligands

Reaction	Complex obtained	Physical properties	Reference
1	2	3	4
$[RuCl_3(PR_3)_2 \cdot MeOH] + MCl$ or $M[RuCl_4(PPh_3)_2] + PR_3$ ($M = Me_4N^+$, Ph_4As^+; $PR_3 = PPh_3$, PMe_2Ph, PEt_3, $P(OPh)_3$)	$M[RuCl_4(PR_3)_2]$	NMR, IR	113, 114
$[RuX_3(AsPh_3)_2 \cdot MeOH] + MX$ ($M = Me_4N^+$, Et_4N^+, Ph_4As^+; $X = Cl$, Br)	$M[RuX_4(AsPh_3)_2]$	NMR, IR	113, 114
$[RuCl_3(EPh_3)_2 \cdot MeOH] + MeNO_2$ ($E = P$, As)	$[RuCl_3(EPh_3)_2(MeNO_2)]$		113, 114
$[RuX_3(EPh_3)_2 \cdot MeOH] + L$ ($X = Cl$, Br; $E = P$, As; $L = CH_3CN$, $C_6H_5CH_2CN$, C_6H_5CN, dmso, thf)	$[RuX_3(EPh_3)_2L]$	NMR, IR	115

contd.

Table I.3 (contd.)

1	2	3	4
[RuX$_3$(EPh$_3$)$_2$.MeOH]+ L (X = Cl, Br; E = P, As; L = bipy, phen, (Me$_2$S)$_2$, (Py)$_2$	[RuX$_3$(EPh$_3$)L]	NMR, IR, Visible	115
[RuCl$_3$(EPh$_3$)$_2$.MeOH]+ CS$_2$ (E = P, As)	[RuCl$_3$(EPh$_3$)$_2$(CS$_2$)]	IR	115
[RuBr$_3$(EPh$_3$)$_2$.MeOH]+ CS$_2$ (E = P, As)	[RuBr$_3$(EPh$_3$)$_2$(CS)]	IR	115
[RuX$_3$(AsPh$_3$)$_2$.MeOH]+ Benzene (X = Cl, Br)	[RuX$_3$(AsPh$_3$)$_2$]	ESR, IR	115
[RuCl$_3$(AsPh$_3$)$_2$.MeOH]+ Zn + cyclopentadiene	[(π-C$_5$H$_5$)Ru(AsPh$_3$)$_2$Cl]		116
[RuCl$_3$(AsPh$_3$)$_3$]+ O$_2$ + Benzene	[RuCl$_3$(AsPh$_3$)(OAsPh$_3$)$_2$]	IR, Visible	112

IR = infrared; NMR = nuclear magnetic resonance; ESR = electron spin resonance.

Ruiz-Ramirez et al.[115] have reported the preparations of a number of ruthenium(III) complexes by the reactions of [RuX$_3$(EPh$_3$)$_2$.MeOH] (X = Cl, Br; E = P, As) with various ligands. One reaction of [RuCl$_3$(AsPh$_3$)$_2$.MeOH] with cyclopentadiene in presence of Zn leading to [(π-C$_5$H$_5$) Ru(AsPh$_3$)$_2$Cl][116] has also been reported.

[RuCl$_3$(AsPh$_3$)$_2$.MeOH] and [RuCl$_3$(PPh$_3$)$_2$.MeOH] have been used as catalysts in the homogeneous reduction of 1-hexene to 1-hexane.[117]

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CHAPTER II

RUTHENIUM(III) AND RUTHENIUM(II) COMPLEXES
CONTAINING TRIPHENYLARSINE AND OTHER LIGANDS

During the last decade a relatively large number of

ruthenium(II) complexes of tertiary phosphines have been syn-

thesized. Some of these have been used as good catalysts[1] for

various reactions e.g., hydrogenation, oxidation, isomerisation

etc. and some, as starting materials[2] for the syntheses of a

wide range of ruthenium(II) complexes. The complexes of ruthe-

nium(III) containing triphenylphosphine and those of ruthenium-

(II) and ruthenium(III) with tertiary mono-arsines are rela-

tively few in number. Besides, practically not much work related

to their utility as catalysts or starting materials has been repor-

ted in the literature. Only a few ruthenium(III) complexes with

tertiary mono-arsines as one of the ligands have been reported.[2-10]

Two new ruthenium(III) compounds viz., $[RuCl_3(AsPh_3)_3]$ and

$[RuCl_3(AsPh_3)(OAsPh_3)_2]$ have been reported.[11] It will, therefore,

be interesting to study the potentialities of these complexes

as starting materials for the syntheses of ruthenium(III) and

ruthenium(II) complexes. This chapter describes the syntheses

of a wide range of ruthenium(III) and ruthenium(II) complexes

containing triphenylarsine as one of the ligands, starting with

the complex $[RuCl_3(AsPh_3)_3]$. It seems that this complex

behaves similar to $[RuCl_3(AsPh_3)_2.MeOH]$ in reactions with

various weakly coordinating ligand molecules. As a result of

a few new interesting reactions some new compounds have been

isolated. These compounds have been characterised by various

physicochemical methods and their geometries have been proposed.

EXPERIMENTAL

All the reagents used were Analar or of chemically pure

grade. All the solvents were freshly distilled before use.

Triphenylarsine, trichloro-tris(triphenylarsine)ruthe-

nium(III) and dichloro-bis(triphenylarsine)ruthenium(II) were

prepared according to the methods described in the literature.[11-13]

Preparations of Complexes and Their Reactions

(i) Preparation of $[RuCl_3(AsPh_3)_2.S]$ (where $S = RCN$ ($R = CH_3$, C_6H_5,
$CH_3CH_2CH_2$, $CH_2=CH$), CH_3NO_2, $C_2H_5NO_2$, Me_2CO, CH_3CHO, C_6H_5CHO,
CS_2, dmf, dmso or thf)

0.2 g of trichloro-tris(triphenylarsine)ruthenium(III)

$[RuCl_3(AsPh_3)_3]$ was taken in minimum amount of the solvent (S)

to dissolve the compound and heated on a water bath for about

5 minutes when a reddish-brown colour appeared and finally the

colour changed to green, red or brown depending on the solvent

used. On cooling the solution, compound started crystallizing

out. The crystals were separated by filtration and washed with

ether and dried under vacuum.

(ii) Preparation of [RuCl$_3$(AsPh$_3$) S$_2$] (where S = pyridine or α-picoline)

The method of synthesis of these compounds was similar to

(i) except that the clear solution, obtained after heating on a

water-bath, was cooled and ether was added to the solution where-

by a precipitate was obtained. It was filtered, washed with

ether and dried under vacuum.

(iii) Preparation of trichloro-bis(triphenylarsine)(carbondisul-phide), [RuCl$_3$(AsPh$_3$)$_2$(CS$_2$)]

0.3 g of trichloro-tris(triphenylarsine)ruthenium(III)

[RuCl$_3$(AsPh$_3$)$_3$] was taken in carbondisulphide (30 ml) and the

solution was refluxed under nitrogen atmosphere for half an

hour. A brown crystalline precipitate was obtained. It was

filtered and washed with carbondisulphide and dried under

vacuum.

(iv) Preparation of [RuCl$_3$(AsPh$_3$) L] (where L=bipy, phen)

Trichloro-tris(triphenylarsine)ruthenium(III) [RuCl$_3$(AsPh$_3$)$_3$] (0.3 g

was dissolved in benzene (20 ml) and the solution was refluxed

with 0.1 g of the ligand (L) under nitrogen atmosphere for half
an hour. A brown coloured compound was obtained. It was fil-
tered, washed with benzene and ether and dried under vacuum.
These compounds were also obtained when the solution of the
ligand and the complex in benzene was stirred at room tempera-
ture for 4 hr.

(v) Preparation of trichloro triphenylarsine-bis(dimethyl-
sulphide)ruthenium(III),$[RuCl_3(AsPh_3)(Me_2S)_2]$

A solution of trichloro-tris(triphenylarsine)ruthenium
(III) $[RuCl_3(AsPh_3)_3]$ (0.2 g) in benzene (20 ml) was treated
with dimethylsulphide (0.8 ml) and the mixture was stirred at
room temperature under nitrogen atmosphere for one hour when
the solution turned red. It was then concentrated on a water-
bath whereby a red compound precipitated out. It was filtered
out and recrystallized from dichloromethane-hexane mixture.

(vi) Preparation of $R_4N[RuX_4(AsPh_3)_2]$ (where R = Me, $X_4 = Cl_4$,
Cl_3Br, Cl_3I and R = Et, $X = Cl_4$)

A slurry of trichloro-tris(triphenylarsine)ruthenium(III)
$[RuCl_3(AsPh_3)_3]$ (0.25 g) was prepared in acetone (30 ml) con-
taining about 1 ml of water. 1.2 g of R_4NX (when R = Me, X = Cl,
Br or I and R = Et, X = Cl) was added to the mixture and stirred
for several hours whereby an orange-red or brown crystalline
compound separated out. The compound was filtered out, washed
successively with acetone, water, ethanol and ether and dried
under vacuum.

(vii) Preparation of $Ph_4As[RuCl_4(AsPh_3)_2].(Me_2CO)_2$

0.15 g of trichloro-tris(triphenylarsine)ruthenium(III)
$[RuCl_3(AsPh_3)_3]$ was suspended in 35 ml of acetone containing
1 ml of conc. HCl and to which 0.1 g of Ph_4AsCl was added. The
mixture was stirred for several hours. The initially brown
coloured solution gave a precipitate of red crystalline com-
pound. It was filtered out, washed successively with acetone,
water, methanol and ether and dried under vacuum.

(viii) Preparation of $[RuCl_2(AsPh_3)_2(RCN)_2]$ where $R = CH_3$,
$CH_3CH_2CH_2$ and $CH_2=CH$)

Trichloro-tris(triphenylarsine)ruthenium(III)$[RuCl_3(AsPh_3)_3]$
(0.2 g) was refluxed with the alkyl nitrile, RCN (10 ml) for
3 hr when a yellow coloured solution was obtained. It was con-
centrated on a water-bath to about 1 ml. On addition of ether
to the cooled concentrated solution resulted in the precipita-
tion of a yellow compound. It was filtered out, washed with
ether and dried under vacuum.

The reactions of $[RuCl_2(AsPh_3)_2]_2$ or $[RuCl_3(AsPh_3)_2.MeOH]$
with the alkyl nitriles yielded $[RuCl_2(AsPh_3)_2(RCN)_2]$ ($R = CH_3$,
$CH_3CH_2CH_2$, $CH_2=CH$).

(ix) Reaction of $Me_4N[RuCl_3X(AsPh_3)_2]$ (X=Cl, Br, I) with CH_3CN

$Me_4N[RuCl_3X(AsPh_3)_2]$ (0.2 g) was dissolved in acetonitrile
(20 ml) and the solution was concentrated on a water-bath when

a green or brown compound separated. It was filtered out and washed with water, ethanol and ether and dried under vacuum. The compounds obtained were of the type $[RuCl_2X(AsPh_3)_2(CH_3CN)]$ $(X = Cl, Br, I)$.

Analyses

The analyses for sulphur and halogens were carried out by the standard methods.[14,15] Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India. The results are reported in Table II.1.

Infrared Spectra

Spectra of the compounds were recorded with a Perkin-Elmer 521 Infrared Diffraction Grating Spectrophotometer in the 4000-300 cm^{-1} range. Samples were prepared as KBr pellets or in Nujol mull.

Conductivity Measurements

Conductivity measurements of the compounds were made on an Elico conductivity meter type CM-80 of millimolar solutions in nitroethane.

Visible Spectra

The electronic spectra were recorded in Nujol mull or in solution using chloroform, acetonitrile or nitroethane as solvents using a Cary Model-14 recording spectrophotometer. The

Table II.1

Analytical data, melting points and colours for ruthenium(III) and ruthenium(II) compounds

Complex	Colour	mp(^{o}C)	A N A L Y S I S							
			Calculated(%)				Found (%)			
			C	H	N	Others	C	H	N	Others
1	2	3	4	5	6	7	8	9	10	11
$RuCl_3(AsPh_3)_2(CH_3CN)$ [a]	Green	194-5	53.01	3.84	1.63		53.4	4.24	1.53	
$RuCl_3(AsPh_3)_2(C_6H_5CN)$ [a]	Green	225(d)	55.95	3.80	1.52		56.0	4.10	1.48	
$RuCl_3(AsPh_3)_2(CH_3CH_2CH_2CN)$	Green	203-5	54.04	4.17	1.57	Cl,12.0	54.3	4.40	1.70	Cl,12.2
$RuCl_3(AsPh_3)_2(CH_2CHCN)$	Green	193	53.65	3.78	1.60		54.1	4.15	1.60	
$RuCl_3(AsPh_3)_2(dmf)$	Orange-red	205	52.44	4.14	1.97	Cl,11.92	52.2	4.10	1.80	Cl,11.6
$RuCl_3(AsPh_3)_2(CH_3CHO)$	Greenish-yellow	162(d)	52.82	3.93	-	Cl,12.32	53.1	4.2	-	Cl,12.5
$RuCl_3(AsPh_3)_2(C_6H_5CHO)$	Green	200	55.77	3.89	-	Cl,11.5	55.5	3.7	-	Cl,11.7
$RuCl_3(AsPh_3)_2(Me_2CO)$ [b]	Brown	205	53.34	4.1	-		53.7	4.3	-	
$RuCl_3(AsPh_3)_2(thf)$ [a]	Orange-red	198(d)	53.86	4.26	-		54.1	4.1	-	
$RuCl_3(AsPh_3)_2(CH_3NO_2)$ [c]	Green	200(d)	50.44	3.75	1.6		50.5	3.9	1.4	
$RuCl_3(AsPh_3)_2(C_2H_5NO_2)$	Brown	185	51.0	3.9	1.57	Cl,11.9	51.3	4.2	1.7	Cl,11.6
$RuCl_3(AsPh_3)_2(dmso)$ [a]	Orange-yellow	198(d)	50.8	4.0	-	Cl,11.87; S,3.57	50.5	3.8	-	Cl,12.1; S,3.7

Table II.1.(contd.)

1	2	3	4	5	6	7	8	9	10	11
$RuCl_3(AsPh_3)_2(CS_2)$ [a]	Brown	260(d)	49.6	3.35	-		49.3	3.3	-	
$RuCl_3(AsPh_3)(py)_2$ [a,b]	Yellow	205(d)	50.0	3.7	4.2		49.7	3.9	4.0	
$RuCl_3(AsPh_3)(\alpha\text{-pic})_2$	Greenish-yellow	165(d)	51.5	4.15	4.05		51.7	4.0	4.15	
$RuCl_3(AsPh_3)(Me_2S)_2$ [a]	Red	176(d)	41.4	4.24	-		41.6	4.1	-	
$RuCl_3(AsPh_3)(bipy)$ [a]	Reddish-brown	239(d)	50.3	3.44	4.2		49.9	3.7	4.7	
$RuCl_3(AsPh_3)(phen)$ [a]	Brown	264	51.93	3.32	4.0		51.8	2.9	4.5	
$Et_4N[RuCl_4(AsPh_3)_2]$ [c]	Orange-brown	218(d)	53.57	5.1	1.42		53.0	4.7	1.4	
$Me_4N[RuCl_4(AsPh_3)_2]$ [c]	Orange-red	262(d)	51.6	4.5	1.5		51.4	4.6	1.3	
$Me_4N[RuCl_3Br(AsPh_3)_2]$	Orange-brown	260(d)	49.3	4.3	1.44	Halogen, 19.14	49.7	4.5	1.4	Halogen, 19.7
$Me_4N[RuCl_3I(AsPh_3)_2]$	Greenish-black	178(d)	47.1	4.2	1.37	Halogen, 22.9	47.5	3.9	1.2	Halogen, 22.1
$Ph_4As[RuCl_4(AsPh_3)_2](Me_2CO)_2$ [c]	Red	195(d)	58.5	4.6	-		58.2	4.5	-	
$RuCl_2Br(AsPh_3)_2(CH_3CN)$	Brown	173	50.4	3.65	1.55	Halogen, 16.66	50.35	3.9	1.7	Halogen, 16.2
$RuCl_2I(AsPh_3)_2(CH_3CN)$	Reddish-brown	160	47.9	3.47	1.47	Halogen, 20.8	47.8	3.7	1.6	Halogen, 20.3

Table II.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
cis-[RuCl$_2$(AsPh$_3$)$_2$(CH$_3$CH$_2$CH$_2$CN)$_2$]	Yellow	170	57.27	4.77	3.0	Cl,7.69	57.5	4.5	3.1	Cl,7.4
cis-[RuCl$_2$(AsPh$_3$)$_2$(CH$_3$CN)$_2$][d]	"	185-7	55.4	4.16	3.23	Cl,8.19	55.2	4.2	3.4	Cl,7.9
cis-[RuCl$_2$(AsPh$_3$)$_2$(CH$_2$=CHCN)$_2$]	"	187	56.6	4.0	3.15	Cl,7.97	56.3	4.2	3.0	Cl,8.2

a, ref. No. 9; b, ref. No. 2; c, ref. No. 7; d, ref. No. 16; dmf, N,N-dimethylformamide; thf, tetrahydrofuran; dmso, dimethylsulphoxide; py, pyridine; α-pic, α-picoline; bipy, N,N'-bipyridyl phen, o-phenanthroline.

results are given in Table II.2.

Magnetic Susceptibility Measurements

These measurements were made using a Gouy-balance at room-temperature ($25^\circ C$). Mercury-tetrathiocyanatocobaltate(II) was used as a calibrant.

Melting Points

Melting points were recorded on a Fisher-Johns melting point apparatus. The results are recorded in Table II.1.

RESULTS AND DISCUSSION

All the compounds were obtained by treating [$RuCl_3(AsPh_3)_3$] (hereafter referred as K) with various ligand molecules. In some cases, the ligands themselves were used as solvents for the reaction while in other cases, the complex K and the ligand were dissolved in a suitable solvent under various conditions. The complex K, seems to have a distorted octahedral geometry.[11] Since, triphenylarsine is a big molecule, there is every possibility of a steric hindrance in the complex when three molecules of triphenylarsine and three chlorine atoms are coordinated to ruthenium atom. Thereby, the complex may be unstable. Thus, on dissolving it in any solvent, there is a possibility of loosing one of the triphenylarsine molecules to give penta-coordinated species, similar to the one obtained from [$RuCl_3(AsPh_3)_2$.MeOH]. This will be discussed further in

Electronic spectral section of this chapter.

The following five types of behaviours are exhibited by the complex K, towards the ligands (L). (i) Displacement of one molecule of triphenylarsine by the ligand to give hexacoordinated ruthenium(III) complexes, [$RuCl_3(AsPh_3)_2L$]. (ii) Displacement of two of the triphenylarsine molecules by the ligand to give hexacoordinated ruthenium(III) complexes, [$RuCl_3(AsPh_3)L_2$]. (iii) Substitution of all the triphenylarsine molecules by the ligand with or without reduction of ruthenium(III) to ruthenium(II) to give complexes of the type [$RuCl_3L_3$] or [$RuCl_2L_4$].[11] (iv) Reduction to ruthenium(II) without complete displacement of triphenylarsine molecules to give [$RuCl_2(AsPh_3)_2L_2$]. (v) Displacement of all the halide ions by pseudohalide ions to give [$RuX_3(AsPh_3)_2$][17] (X = pseudohalogen). The complex K, on treatment with tetraalkyl or aryl ammonium or arsonium salts in proper solvent gives the anionic ruthenium(III) complexes, R_4M[$RuX_4(AsPh_3)_2$].

The reactions of R_4M[$RuCl_3X(AsPh_3)_2$] (X = Br or I) with acetonitrile are also very interesting. In these reactions, compounds of the type [$RuCl_2X(AsPh_3)_2(CH_3CN)$] and not [$RuCl_3(AsPh_3)_2(CH_3CN)$] were obtained. [$RuCl_3(AsPh_3)_2(CH_3CN)$] was obtained only when R_4M[$RuCl_4(AsPh_3)_2$] was treated with acetonitrile. In case of mixed halogen anionic ruthenium(III) complexes, only the mixed halide complexes were obtained.

When K is dissolved either in a coordinating or a non-coordinating solvent first the colour of the solution was reddish brown which then changed to the colour of the resulting complex. Thus when K was dissolved in acetonitrile, a reddish brown solution was first obtained which on warming further on a water-bath for sometime, changed to green from which green crystals of $[RuCl_3(AsPh_3)_2(CH_3CN)]$ were obtained. Again the same redsish brown solution was obtained when K was dissolved in benzene. If a few drops of acetonitrile were added to this reddish brown solution in benzene and then warmed on a water-bath for sometime, a green solution which gave the green crystals $[RuCl_3(AsPh_3)_2(CH_3CN)]$ was obtained. Similar behaviour was observed in nearly all the reactions which gave compounds of the type $[RuCl_3(AsPh_3)_2L]$. One can, therefore, tentatively think that all the reactions of $[RuCl_3(AsPh_3)_3]$ underwent by the S_N1 mechanism according to the following scheme:

$[RuCl_3(AsPh_3)_3]$ + Solvent $\rightleftharpoons$ $[RuCl_3(AsPh_3)_2]$ + $AsPh_3$ + Solvent

(Reddish-brown solution)

$\downarrow$ Ligand (L)
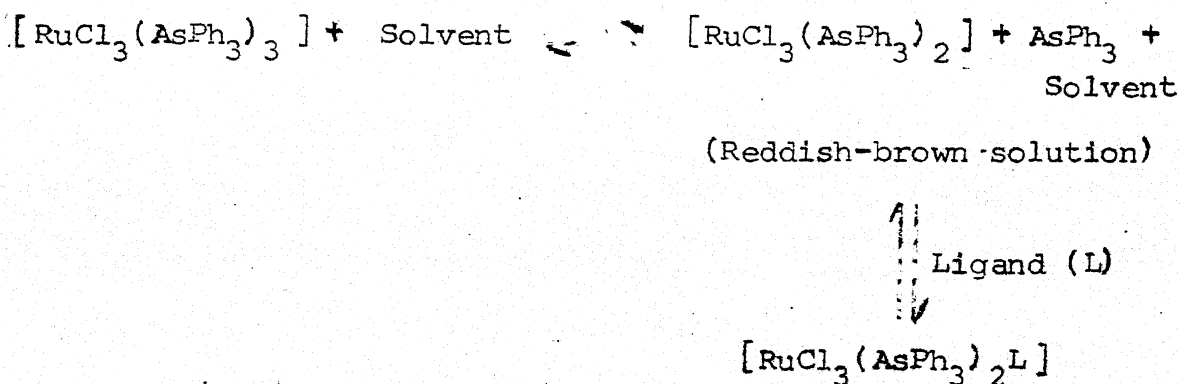
$[RuCl_3(AsPh_3)_2L]$

In the cases, where compounds of the type $[RuCl_3(AsPh_3)L_2]$ are

obtained, the first step could be the formation of penta-coor-
dinated species, [$RuCl_3(AsPh_3)_2$] which reacts with the ligand
to give the monosubstituted product first and subsequently,
due to more affinity of ruthenium(III) for the ligand L, or
due to the chelate effect of the bidentate ligands, another
molecule of triphenylarsine is knocked off to give [$RuCl_3(AsPh_3)L_2$]
or [$RuCl_3(AsPh_3)L'$] (where L and L' are mono- and bidentate
ligands respectively).

Different products obtained by the reactions of the com-
plex K with the ligands depend on the nature of the ligand and
the various conditions used. Here, the results and discussions
are presented under the ligand headings for the convenience of
discussions.

Nitrogen Ligands

(a) Alkyl and aryl cyanides

Syntheses of some alkyl and aryl cyanide complexes with
ruthenium(II) and ruthenium(III) having tertiary phosphines or
arsines are reported in the literature.[9,16,18,19] Complexes of
the type [$RuX_3(AsPh_3)_2(RCN)$] (X = Cl or Br; R = Me, $PhCH_2$, Ph or
CH_2CH) are reported to have been prepared using [$RuCl_3(AsPh_3)_2$.-
MeOH] and the corresponding nitriles.[9]

The green compounds [$RuCl_3(AsPh_3)_2(RCN)$] (R = Me, Ph, CH_2=CH,
$CH_3CH_2CH_2$), obtained as a result of the reaction of [$RuCl_3(AsPh_3)_3$]
with RCN are non-electrolyte in nitroethane and have magnetic

moments in the range 1.8 to 1.9 B.M. These properties indicate that they are non-ionic and spin-paired ruthenium(III) complexes. The behaviours of few such compounds (R = Me, Ph) which are reported earlier[9] are in conformity with the ones prepared by us. The infrared spectra of these complexes in nujol mull showed a weak band in the range 2320-2280 cm^{-1} which is assigned to the stretching mode of C≡N group coordinated to ruthenium-(III) through the nitrogen atom. Similar results have been reported in the case of other alkyl or aryl nitrile substituted triphenylphosphine and triphenylarsine complexes of ruthenium(II) and ruthenium(III).[9,16,18,19] In the case of benzonitrile complex, characteristic and split bands due to the phenyl groups (present both in benzonitrile and triphenylarsine) around 1580, 1480, 1435, 750 and 695 cm^{-1} were present. The splitting of the bands may be due to the presence of two different type of phenyl groups present in the complex.

Under ordinary conditions, the nitriles could replace only one out of the three triphenylarsine molecules present in K without the reduction of ruthenium(III). However, prolonged reaction of K with the nitriles gave the ruthenium complex, [$RuCl_2(AsPh_3)_2(RCN)_2$]. Similar compounds were obtained when [$RuCl_2(AsPh_3)_2$]$_2$ or [$RuCl_3(AsPh_3)_2$·MeOH] was treated under reflux with the nitriles for about 3 hr. The ruthenium(II) dinitrile complexes, obtained from all the three compounds, [$RuCl_3(AsPh_3)_3$], [$RuCl_3(AsPh_3)_2$·MeOH] and [$RuCl_2(AsPh_3)_2$]$_2$

are similar in all respects. The infrared spectra of these dinitrile complexes showed two infrared bands in the region 2320-2150 cm^{-1}. The acetonitrile complex showed bands at 2320 and 2260 cm^{-1} whereas the butyronitrile complex had absorptions at 2270 and 2250 cm^{-1}. These bands could very safely be assigned to ν_{CN} for the cis-geometry of the nitrile complexes in analogy with similar other cis-complexes,[16,18] Thus, it appears that in these dinitrile complexes, the nitrile groups are in cis position. The infrared absorptions in the case of the acrylonitrile complex showed lower values (2240 and 2210 cm^{-1}) of the ν_{CN} band positions. Here as well, one can assign them for the cis-isomer, but the reason for such a low energy for ν_{CN} in this nitrile is not known. All these ruthenium(II) complexes have a marked similarity in being yellow in colour whereas all the nitrile complexes of ruthenium(III) are green. The cis-acetonitrile complex, [$RuCl_2(AsPh_3)_2(CH_3CN)_2$] has been reported earlier from [$RuCl_2(AsPh_3)_2]_2$[16] Our observations of getting ruthenium(II) nitrile complexes from [$Ru(AsPh_3)_3Cl_3$] or [$RuCl_3(AsPh_3)_2$.MeOH] are not in conformity with the results obtained by L. Ruiz-Ramirez, et al.[9] They could isolate similar compounds only with the triphenylphosphine analogue,[$RuX_3(PPh_3)_2$.MeOH] and RCN and not with [$RuX_3(AsPh_3)_2$.MeOH] and RCN. All these ruthenium(II) complexes are found to be diamagnetic. Isolation of a similar ruthenium(II) complex with benzonitrile was not possible.

(b) Pyridine, α -Picoline, N,N'-bipyridyl and 1,10-phenanthroline

The compounds obtained from the reactions of K with these amines are of the type, [$RuCl_3(AsPh_3)L_2$] (L = py or α-picoline) or [$RuCl_3(AsPh_3)L_2'$] (L_2' = bipy or phen). The monosubstituted product in the case of pyridine and α-picoline could not be obtained. Probably the monosubstituted product is formed first, but due to the strong trans-effect of pyridine or picoline another triphenylarsine molecule is also substituted by the ligand. In the case of bidentate ligands bipy or phen owing to the chelate effect, substitution of two triphenylarsine molecules by one ligand molecule takes place. The reaction of K with pyridine has been described in detail earlier.[11] Apart from getting [$RuCl_3(AsPh_3)(py)_2$] from [$Ru(AsPh_3)_3Cl_3$] and pyridine, compounds of the type [$Ru(Py)_3Cl_3$] & [$Ru(Py)_4Cl_2$] were also obtained when the reaction was carried out for longer period. The infrared spectra of all these compounds showed absorptions both due to triphenylarsine and the corresponding amines. The pyridine, N,N'-bipyridyl and 1,10-phenanthroline complexes were reported earlier by the reactions of [$RuCl_3(AsPh_3)_2MeOH$] with the corresponding amines.[9]

Oxygen Ligands

(a) Ketones

The reaction of K with acetone gives [$RuCl_3(AsPh_3)_2(Me_2CO)$]. Here, one of the labile triphenylarsine molecule of K is easily

substituted by the ketone. However, attempts to isolate a similar compound with ethyl emthyl ketone and acetophenone were unsuccessful. In the case of acetone the complex K was first dissolved completely in the boiling solvent from which on cooling the crystals of the complex separated out. In the case of ethyl methyl ketone and acetophenone, the complex did not separate out even on concentration and cooling. Attempts to precipitate the complex by the addition of ether resulted in a compound which could be the decomposed products containing mainly $[RuCl_3(AsPh_3)_2]$. The C, H analyses were very close to the formula $[RuCl_3(AsPh_3)_2]$. The infrared spectra conformed the observations. In the case of acetone complex, a strong band at 1655 cm^{-1} was observed which was assigned to the coordinated $\nu_{C=O}$ group (free $\nu_{C=O}$ in acetone is observed at 1725 cm^{-1}). No band in the region 1800-1600 cm^{-1} was observed in the spectra of the product obtained in the case of acetophenone and ethyl methyl ketone. It could possibly be that ethyl methyl ketone and acetophenone form relatively weaker bonds and upon the addition of ether, the weakly coordinated ligand is set free and a pentacoordinate species $[RuCl_3(AsPh_3)_2]$ is obtained. This pentacoordinated species is characterised mainly by the electronic spectra (discussed in detail later). The acetone complex is similar in properties to the one obtained by Stephenson, et al.[2]

(b) Aldehydes

The aldehydes behave similar to acetone. Green crystals of the complexes [RuCl₃(AsPh₃)₂L] (L = acetaldehyde or benzaldehyde) were obtained when K was treated with the corresponding aldehyde. The aldehyde complexes seem to be more stable compared to the keto complex. This type of complexes containing an aldehyde and triphenylarsine as ligands are being reported for the first time. The infrared spectra of the complexes confirmed the presence of a carbonyl group. $\nu_{C=O}$ due to coordinated carbonyl groups is observed at 1650 and 1620 cm^{-1} in the case of acetaldehyde and benzaldehyde complexes respectively. In the case of benzaldehyde complex the characteristic bands due to phenyl group (present both in benzaldehyde and triphenylarsine) at 1600, 1575, 1480, 1445, 1435 cm^{-1} were observed. Each of the bands at 740 and 470 cm^{-1} were split into three bands 750, 740, & 730 cm^{-1} and 480, 470, & 455 cm^{-1} respectively. These compounds showed paramagnetism due to one unpaired electron (μ_{eff} = 1.8 B.M.) confirming ruthenium being present in +3 oxidation state in the complexes.

(c) N,N-Dimethylformamide (dmf):

The compound obtained by the reaction of K and dmf is similar to the one obtained from aldehydes viz.,[RuCl₃(AsPh₃)₂(dmf)]. The infrared spectrum of the complex shows a strong band at

1640 cm^{-1} which is assigned to the coordinated $\nu_{C=O}$ group (ν_{CO} in the spectrum of dmf appears at 1700 cm^{-1}). This shows that the coordination is not through the nitrogen atom but through the oxygen atom of the carbonyl group. Another band is observed at 1360 cm^{-1} corresponding to a 1410 cm^{-1} band present in the spectrum of dmf. This band is due to the C-N vibrational mode. The compound shows paramagnetism equivalent to one unpaired electron indicating the presence of ruthenium in +3 state in the compound.

(d) Tetrahydrofuran (thf)

On warming K with thf for about 5 min. on a water-bath, crystals of [RuCl$_3$(AsPh$_3$)$_2$(thf)] were obtained. This compound is similar to the one obtained by treating [RuCl$_3$(AsPh$_3$)$_2$.MeOH] with thf reported by Ruiz Ramirez, et al.[9]

(e) Dimethyl sulphoxide (dmso)

Treating K with dmso under the similar conditions as those in the case of thf, [RuCl$_3$(AsPh$_3$)$_2$(dmso)]was obtained. The coordination of the ligand to the metal ion is through the oxygen atom and not through the sulphur atom, since the infrared spectrum in nujol mull shows bands at 980, 945 and 930 cm^{-1}. The band at 930 cm^{-1} is strong and sharp and can be assigned to $\nu_{S=O}$ bonded through O-atom (dmso absorbs at 1100-1055 cm^{-1}). Similar results were reported by Ruiz-Ramirez, et al.[9] where they obtained this compound from [RuCl$_3$(AsPh$_3$)$_2$.MeOH].

(f) Nitroalkanes and nitrobenzene

When K was treated with nitromethane or nitroethane under the conditions similar to those in the case of thf, crystalline compound [$RuCl_3(AsPh_3)_2L$] ($L = CH_3NO_2$ or $C_2H_5NO_2$) separated out. The nitromethane compound has been reported to have been prepared by Stephenson from [$RuCl_3(AsPh_3)_2$.MeOH].[7] The infrared spectra of the compounds show one band at 1550 cm^{-1} which can be assigned to the symmetric stretching frequency of the nitro-group which was not observed by Stephenson.[7] In the case of nitrobenzene, the results were similar to those of acetophenone and ethyl methyl ketone (discussed earlier). The compound obtained analysed nearly for [$RuCl_3(AsPh_3)_2$]. It seemed to contain small amount of the nitrobenzene complex also, since infrared spectrum of the product showed a very weak band at 1520 cm^{-1} which might be due to the symmetric stretching frequency of the nitro group.

Sulphur Ligands

Reaction of K with CS_2 and dimethyl sulphide gave compounds viz., [$RuCl_3(AsPh_3)_2(CS_2)$] and [$RuCl_3(AsPh_3)(Me_2S)_2$] respectively. These are similar to the compounds obtained by Ruiz-Ramirez et al.[9] from [$RuCl_3(AsPh_3)_2$.MeOH]. The carbon disulphide complex shows a band at 1510 cm^{-1} (CS_2 shows a band at 1500 cm^{-1}) which is indicative of linearly bound CS_2 group. The CS_2 group is not lost ordinarily at room temperature. But the compound on

grinding for a long period slowly starts losing CS_2 (evidence from electronic spectrum in nujol mull to be discussed later). The dimethyl sulphide complex is fairly stable (even on recrystallization, the coordinated solvent is not liberated).

Reactions with tetra alkyl or aryl-ammonium or arsonium salts

When K was treated with tetra-alkyl ammonium salts of the type R_4NX (where R = Me, X = Cl, Br, I and R = Et, X = Cl) in a solvent like acetone, complexes of the type $R_4N[RuX_4(AsPh_3)_2]$ (where R = Me, $X_4 = Cl_4$, Cl_3Br or Cl_3I or R = Et, $X_4 = Cl_4$) were obtained. The interesting aspect of these reactions is the formation of mixed halogeno anionic complexes. Complexes of the type $R_4N[RuX_4(AsPh_3)_2]$ (where R = Me; X = Cl or Br and R = Et, X = Cl) have been synthesized by Stephenson[7] using $[RuX_3(AsPh_3)_2 \cdot MeOH]$ and the corresponding tetra-alkyl halides. The treatment of K with Ph_4AsCl in acetone gave a complex $Ph_4As[RuCl_4(AsPh_3)_2] \cdot 2(Me_2CO)$ which has also been reported by Stephenson[7] from $[RuCl_3(AsPh_3)_2 \cdot MeOH]$. Two molecules of acetone present in the lattices of the crystal show an infrared absorption at 1715 cm^{-1}. This band is assigned to $\nu_{C=O}$ of the uncoordinated acetone molecules. A possible explanation for the formation of the complex with two acetone molecules in the lattice has been furnished by Stephenson.[7] Infrared spectra of other tetra-alkyl anionic ruthenium(III) complexes did not show any special feature in the range 4000-300 cm^{-1}. ν_{M-X} (X = Br or I) in the case of mixed halogeno

complex is expected at a lower energy than 300 cm^{-1}. Hence, no new absorptions were observed. All the complexes showed conductivity in nitroethane corresponding to 1:1 electrolyte. The values of Λ_M were of the order of 70 ohm^{-1}cm^{2}mol^{-1}. Only in the case of tetraphenylarsonium compound it was little low (45 ohm^{-1}cm^{2}mol^{-1}).

Reactions of Me$_4$N[RuCl$_3$X(AsPh$_3$)$_2$] (X = Br, I) with acetonitrile

When the mixed halogeno anionic complexes, Me$_4$N[RuCl$_3$X(AsPh$_3$)$_2$] (X = Br, I) were dissolved in acetonitrile and concentrated on a water-bath, compounds of the type [RuCl$_2$X(AsPh$_3$)$_2$(CH$_3$CN)] (X = Br, I) were obtained. When X = Cl was taken, the product obtained was a green compound[RuCl$_3$(AsPh$_3$)$_2$(CH$_3$CN)] similar to the one obtained by the reaction of [RuCl$_3$(AsPh$_3$)$_3$] and acetonitrile. In case of X = Br and I, the compounds obtained had brown and dark reddish brown colours respectively. These complexes are non-electrolytes in nitroethane. The method of obtaining mixed halogeno complexes can be extended to systems where a halide could be substituted by solvent like nitromethane (Stephenson[7] obtained [RuCl$_3$(AsPh$_3$)$_2$(CH$_3$NO$_2$)] from R$_4$M[RuCl$_4$(AsPh$_3$)$_2$] and nitromethane). The infrared spectra of the bromo- and iodo-complexes showed a weak band at 2305 cm^{-1} and 2300 cm^{-1} respectively assignable to the ν_{CN} of the coordinated acetonitrile.

ELECTRONIC SPECTRA

These compounds in general gave two types of electronic

spectra in the range 1000-340 nm. In one, the positions of the

bands were around 620, 450, 400 and 350 nm whereas in the others,

around 900, 520, 410 and 350 nm (Table II.2). Besides in a few

cases bands around 900, 600, 500, 400 and 350 nm were also pre-

sent. Since in a d^5 system, and especially in ruthenium(III)

which has relatively high oxidising properties, the charge trans-

fer bands of the type $L_{\pi y} \rightarrow {}^2t_{2g}$ are prominent[20] in the low

energy region which obscure the weaker bands due to d-d transi-

tion. It, therefore, becomes difficult to assign conclusively

the bands of ruthenium(III) complexes which appear in the visible

region. However, the extinction coefficient of the band around

600 nm in all the complexes was found to be of the order of 500,

while those of the other bands were much higher. On the basis

of the extinction coefficient, the band at 620 nm is assigned to

the ligand field transition $({}^2T_{2g} \rightarrow {}^2T_{1g}$ or ${}^2A_{2g})$.[21] It is

equally possible that this band may be due to the components of

symmetry forbidden charge transfer transition as predicted by

Jørgensen[22] for $[IrCl_6]^{2-}$. Other bands which appear around 500,

450 and 400 nm can be assigned to charge transfer bands of the

type $L_{\pi y} \rightarrow {}^2t_{2g}$, as suggested by the high value of the extinc-

tion coefficient.[20]

In the foregoing paragraphs reference has been made of the

possible formation of pentacoordinated species. It is assumed

Table II.2

Electronic spectral data of the complexes[a]

Sl. No.	Complex	λ max nm	ε	Assignment
1	2	3	4	5
1.	$RuCl_3(AsPh_3)_2(CH_3CN)$	860	25	—
		618	140	$^2T_{2g} \rightarrow {}^2A_{2g}$
		440	1400	Charge Transfer
		395	3620	"
		350sh	—	"
2.	$RuCl_3(AsPh_3)_2(CH_3CH_2CH_2CN)$	830	45	—
		620	160	$^2T_{2g} \rightarrow {}^2A_{2g}$
		450sh	1280	Charge Transfer
		397	2900	"
		350sh	—	"
3.	$RuCl_3(AsPh_3)_2(CH_2=CHCN)$	900	85	—
		637	140	$^2T_{2g} \rightarrow {}^2A_{2g}$
		400	3260	Charge Transfer
		350sh	—	"
4.	$RuCl_3(AsPh_3)_2(C_6H_5CN)$	640	580	$^2T_{2g} \rightarrow {}^2A_{2g}$
		390	2900	Charge Transfer
		350sh	—	"
5.	$RuCl_3(AsPh_3)_3$	910	480	—
		520	1000	$^2T_{2g} \rightarrow {}^2A_{2g}$
		400	2060	Charge Transfer
		350sh	—	"

Table II.2 (contd.)

1	2	3	4	5
6.	$RuCl_3(AsPh_3)_2$	910	450	–
		520sh	1230	$^2T_{2g} \rightarrow {}^2A_{2g}$
		410	2450	Charge Transfer
		350sh	–	"
7.	$RuCl_3(AsPh_3)_2(dmf)$	900	60	–
		515sh	440	$^2T_{2g} \rightarrow {}^2A_{2g}$
		410	1710	Charge Transfer
		350sh	3160	"
8.	$RuCl_3(AsPh_3)_2(dmf)^b$	910	43	–
		–	–	–
		410	1450	Charge Transfer
		360	4620	"
9.	$RuCl_3(AsPh_3)_2(dmso)$	860	80	–
		555	315	$^2T_{2g} \rightarrow {}^2A_{2g}$
		410	1300	Charge Transfer
		350	1950	"
10.	$RuCl_3(AsPh_3)_2(Me_2CO)$	900	770	–
		520sh	750	$^2T_{2g} \rightarrow {}^2A_{2g}$
		410	1740	Charge Transfer
		350sh	–	"
11.	$RuCl_3(AsPh_3)_2(CH_3CHO)$	910	430	–
		520sh	840	$^2T_{2g} \rightarrow {}^2A_{2g}$
		414	1860	Charge Transfer
		350sh	–	"

Table II.2 (contd.)

1	2	3	4	5
12.	$RuCl_3(AsPh_3)_2(C_6H_5CHO)$	900	280	–
		520sh	845	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		413	1820	Charge Transfer
		350sh	–	"
13.	$RuCl_3(AsPh_3)_2(C_6H_5CHO)^b$	910	8	–
		535sh	50	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		412	1150	Charge Transfer
		362	3920	"
14.	$RuCl_3(AsPh_3)_2(CH_3NO_2)$	900	260	–
		600	180	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		395	2920	Charge Transfer
		350sh	–	"
15.	$RuCl_3(AsPh_3)_2(CH_3NO_2)^b$	900	42	–
		530sh	80	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		412	1600	Charge Transfer
		362	4910	"
16.	$RuCl_3(AsPh_3)_2(C_2H_5NO_2)$	900	800	–
		500sh	855	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		400	1245	Charge Transfer
		350sh	1650	"
17.	$RuCl_3(AsPh_3)_2(thf)$	810	210	–
		510	800	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		405	1800	Charge Transfer
		345sh	–	"

Table II.2 (contd.)

1	2	3	4	5
18.	$RuCl_3(AsPh_3)_2(CS_2)$	900	405	–
		–	–	–
		425	1560	Charge Transfer
		360sh	–	"
19.	$RuCl_3(AsPh_3)(Py)_2$	–	–	–
		450	2000	Charge Transfer
		393	3780	"
20.	$RuCl_3(AsPh_3)(bipy)$	550	1260	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		445sh	2580	Charge Transfer
		387	5200	"
21.	$Me_4N[RuCl_4(AsPh_3)_2]^c$	510sh	300	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		448	810	–
		392	4420	Charge Transfer
		379	4240	"
		353	3710	"
22.	$Ph_4As[RuCl_4(AsPh_3)_2](Me_2CO)_2^c$	510sh	325	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		447	920	–
		392	4560	Charge Transfer
		380	4350	"
		354	3710	"

a, in chloroform solution except where indicated,
b, in dmf,
c, in nitroethane.

here that the first type of the spectra (620, 450, 400 and 350 nm) was due to the presence of hexacoordinated species while the second type of the spectra arose due to the presence of pentacoordinated species or pentacoordinated species in equilibrium with the hexacoordinated species. The absence of the band around 620 nm in the spectra of the second type may be due to the shift in equilibrium mostly towards pentacoordinated species with the result, the concentration of the hexacoordinated species is so small that no band appears in 600 nm region. This assumption is based on the following observations.

The Nujol mull spectrum of $[RuCl_3(AsPh_3)_2]$[9] which has been shown to have square pyramidal structure in the solid state and trigonal bipyramidal in solution[10] showed a band at 920 nm whereas $[RuCl_3(AsPh_3)_3]$ having octahedral geometry showed no band under the same condition in this region. In chloroform solution, the spectra of the compounds $[RuCl_3(AsPh_3)_2]$ and $[RuCl_3(AsPh_3)_3]$ were identical and showed bands at 910, 520(sh), 410 and 350 nm (sh). The values of extinction coefficients for these bands were also quite comparable in both the cases (Fig. II.1). This indicates that the presence of a band in the 900 nm region is possibly suggestive of the presence of pentacoordinated species. One could, therefore, assume that $[RuCl_3(AsPh_3)_3]$ which has an octahedral geometry in the solid state[11] dissociates to pentacoordinated species $[RuCl_3(AsPh_3)_2]$ in solution.

Similarly the spectrum of CS_2 complex, $[RuCl_3(AsPh_3)_2(CS_2)]$ taken in Nujol mull showed a band at 920 nm whereas the spectra of dmf and benzaldehyde complexes $[RuCl_3(AsPh_3)_2(dmf)]$ and $[RuCl_3(AsPh_3)_2(C_6H_5CHO)]$ in Nujol mull did not show any band in this region. This could be explained by the fact that the bond between CS_2 and ruthenium might be very weak as CS_2 is not a good donor ligand and in the solid state the complex is dissociated. With the result, the presence of pentacoordinated species might be responsible for the band around 900 nm. However, the complexes of dmf and benzaldehyde are not dissociated at all in the solid state. This is also in conformity with their spectra in chloroform solution where the benzaldehyde and dmf complexes showed bands in the 900 nm region. Further in the spectrum of the CS_2 complex, the 900 nm band is more intense as compared to the ones in the dmf and benzaldehyde complexes.

The presence of equilibrium that exist between the penta- and hexa-coordinated species was further confirmed by the study of the spectra of complexes under different conditions. Thus, in the spectrum of dmso complex when taken in chloroform solution after refluxing for one hour, the intensity of the band at 860 nm is enhanced by two fold relative to that in the spectrum of the solution without refluxing.

Another evidence from which the presence of pentacoordinated species could be surmised was obtained from the electronic spectra of some of the complexes taken in a non-coordinating

solvent like chloroform and in a coordinating solvent like dmf. Thus, the intensity of 910 nm band for the dmf complex in dmf was lower (43) relative to the one when the spectrum was taken in chloroform (60). It was further lowered to 25 after keeping the solution for about 2 hr and finally the band disappeared when the spectrum was taken after 24 hr. In the case of the spectrum of benzaldehyde complex in chloroform, the intensity of 900 nm band was relatively large whereas in dmf solution the 910 nm band was scarcely visible and it was completely disappeared when the spectrum was recorded after 24 hr for the same solution. Similar observations were also obtained with the nitromethane complex in dmf (Table II.2).

Thus, from the above experimental results it appears that the spectra of the first type are probably due to hexacoordinated species of the complex present in solution while those of the second type due to the presence of the pentacoordinated species formed as a result of partial dissociation of hexacoordinated species. Since on lowering the symmetry of the field from O_h to C_{4v} (square pyramidal) or D_{3h} (trigonal bipyramidal) the T terms will be split into one non-degenerate (B or A) and other doubly degenerate (E) terms, one could expect a band due to d-d transition on the low energy side. It is also probable that due to lower value of the extinction coefficient of the 900 nm band, this band may arise due to one of the spin forbidden transitions under C_{4v} or D_{3h} symmetry. The pentacoordinated species

may have either square pyramidal or trigonal bipyramidal struc-
ture. However, the square pyramidal geometry is preferred over
trigonal bipyramidal because in all the reactions studied it
appears that one ligand molecule simply replaces one triphenyl-
arsine molecule from $[RuCl_3(AsPh_3)_3]$ and if S_N1 mechanism is
assumed, square pyramidal geometry will provide minimum rearrange-
ment of the other coordinated ligand molecules.

From the above discussion it is assumed that an equili-
brium of the type shown below between hexa- and penta-coordina-
ted species is established in solution:

$$[RuCl_3(AsPh_3)_2L] \rightleftharpoons [RuCl_3(AsPh_3)_2] + L$$
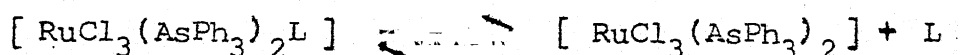
In all the cases, the extent of dissociation depends on the
solvent used.

Thus, on the basis of the above equilibrium, the intensity
of the band around 900 nm may qualitatively give some idea of
the amount of dissociation of the octahedral species into penta-
coordinated species in solution. The presence of bands charac-
teristic of both penta- and hexa-coordinated species could be
explained as follows. Assume that the equilibrium between the two
species is not shifted preferentially to either one direction.
With the result, the concentration of both the species present
in solution was high enough so as to give bands characteristic
of both.

A few examples of complexes having this type of spectra
are given below:

Bands both around 900 nm and 620 nm were observed in the
spectra of alkyl nitrile complexes of ruthenium(III) in chloro-
form solution. The relative intensities of the bands were low (Fig.II.2 &
Table II.2). In the spectrum of benzonitrile complex taken in
chloroform solution, band at 900 nm was absent. It indicates
that the bonding by benzonitrile is stronger as compared to
acrylo, aceto or butyronitrile in whose spectra, both bands
around 900 and 600 nm were present. So in the benzonitrile
complex the dissociation to the corresponding pentacoordinated
species was negligible and the intensity for the band at 640 nm
was high as compared to the other nitrile complexes ($\epsilon = 25-85$)

The electronic spectra of most other complexes, viz.,
$[RuCl_3(AsPh_3)L]$ (L = dmf, dmso, Me_2CO, CH_3CHO, C_6H_5CHO, $C_2H_5NO_2$,
thf and CS_2) were very much similar in chloroform solution. All
of them showed two bands around 900 and 410 nm and two shoulders
or bands around 520 and 350 nm. No band appeared at 620 nm. The
absence of 620 nm band shows that the concentration of octahedral
species in solution is negligible. The values of the extinction
coefficients of 900 nm band in all these complexes are in the
range of 210 to 800 except for dmf and dmso complexes ($\epsilon = 60-80$).
The high intensity of 900 nm band in all these complexes show
that the dissociation to the pentacoordinate species is very
high.

In the spectra of the ruthenium(III) complexes which re-
tained their octahedral geometry in solution, there are a few
interesting observations. The α, α'-bipyridyl complex
$[RuCl_3(AsPh_3)(bipy)]$ showed two bands and a shoulder at 550,
445(sh) and 387 nm in chloroform solution. The positions of
all these bands were shifted slightly towards lower wavelength
compared to the other octahedral ruthenium(III) complexes.
Manoharan et al.[10] observed bands at 408 and 347 nm for
$[RuCl_3(AsPh_3)_2.MeOH]$ and $Et_4N[RuCl_4(AsPh_3)_2]$ in methanol solu-
tion in the visible region. However, our study indicates that
besides these bands one more band is present at 620 nm for
$[RuCl_3(AsPh_3)_2.MeOH]$ complex in methanol.[11] It seems that the
band at 408 nm is shifted to lower wavelength (≈ 20 nm) in case
of the bipyridyl complex and the band at 347 nm is shifted
towards uv region. The band at 620 nm too has shifted to lower-
wavelengths and split up into two at 550 and 445 nm (sh). This
may be due to the lowering of symmetry in the case of $[RuCl_3(AsPh_3)-$
(bipy)] as compared to that of $[RuCl_3(AsPh_3)_2.MeOH]$.

Due to the low solubility of tetramethyl ammonium and tetra-
phenylarsonium salts of $[RuCl_4(AsPh_3)_2]^-$ in chloroform their
spectra were taken in nitroethane and acetonitrile. The salts,
$R_4N[RuCl_4(AsPh_3)_2]$ (R = Me, Et) in acetonitrile, gave spectra
similar to that of $[RuCl_3(AsPh_3)_2(CH_3CN)]$ in chloroform solution.
Bands at 620, 445(sh), 395 and 350 nm (sh) were observed which
agree quite well with octahedral ruthenium(III). The band at

860 nm for $[RuCl_3(AsPh_3)_2(CH_3CN)]$ in chloroform, was, however, not present as no pentacoordinate species was expected to be present in acetonitrile solution. The salts dissolve in aceto-nitrile with a change in colour from orange to green and the appearance of the spectrum of $[RuCl_3(AsPh_3)_2(CH_3CN)]$. The electronic spectra of the tetramethyl ammonium and tetraphenyl-arsonium salts of $[RuCl_4(AsPh_3)_2]^-$ anion in nitroethane were almost superimposable. The extinction coefficients, band posi-tions and the nature of the bands were very much alike. (Fig.II.3).

Fig.II.1 ELECTRONIC SPECTRA

The y-axis is labeled EXTINCTION COEFFICIENT with values 4000, 3500, 3000, 2500, 2000, 1500, 1000, 162, 150, 125, 100, 75, 50, 25. The x-axis is labeled WAVELENGTH, nm with values 300, 400, 500, 600, 700, 800, 900, 1000.

Legend:
① $[RuCl_3(AsPh_3)_2(CH_3CN)]$
② $[RuCl_3(AsPh_3)_2(CH_3CH_2CH_2CN)]$
③ $[RuCl_3(AsPh_3)_2(CH_2=CHCN)]$
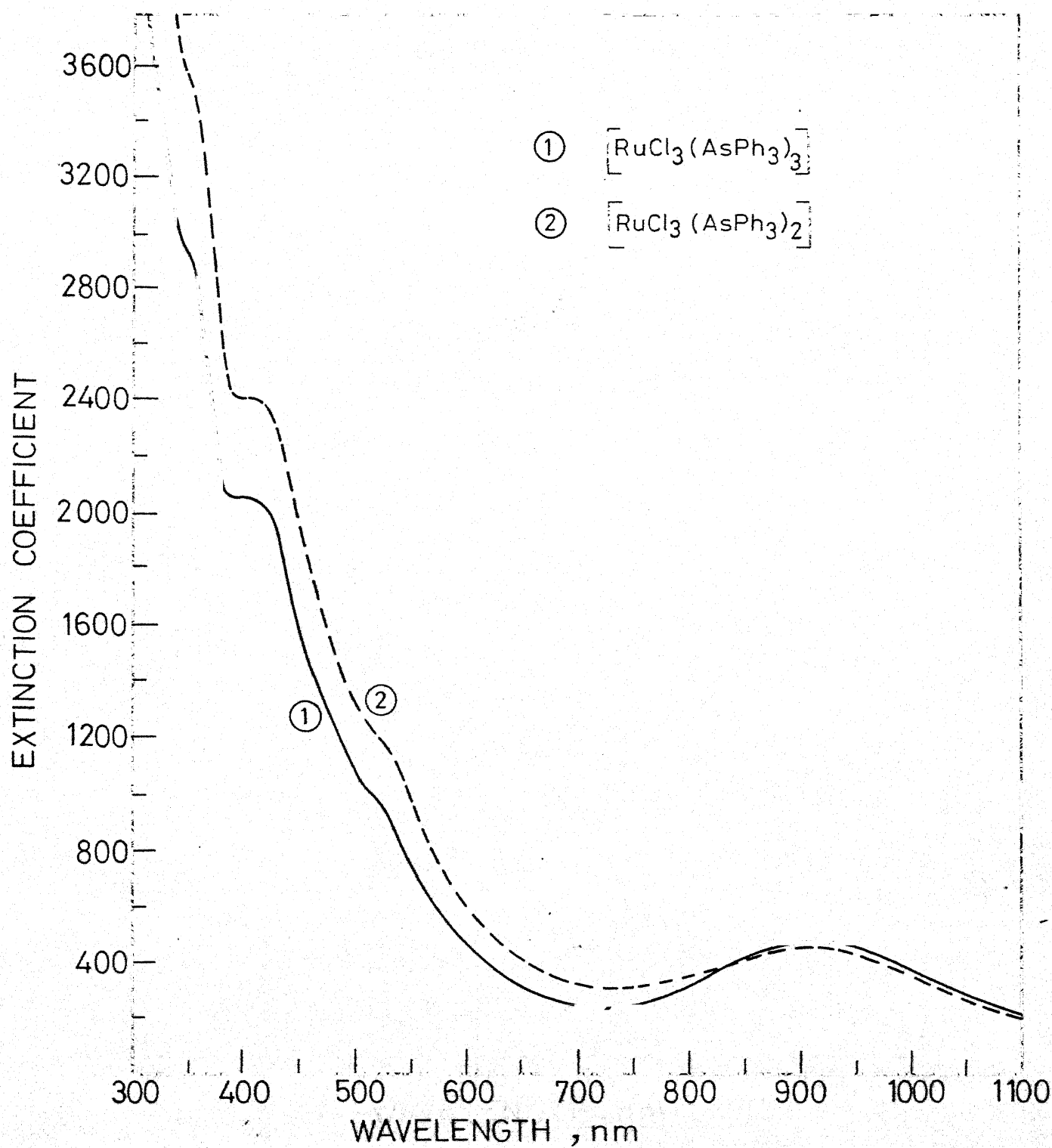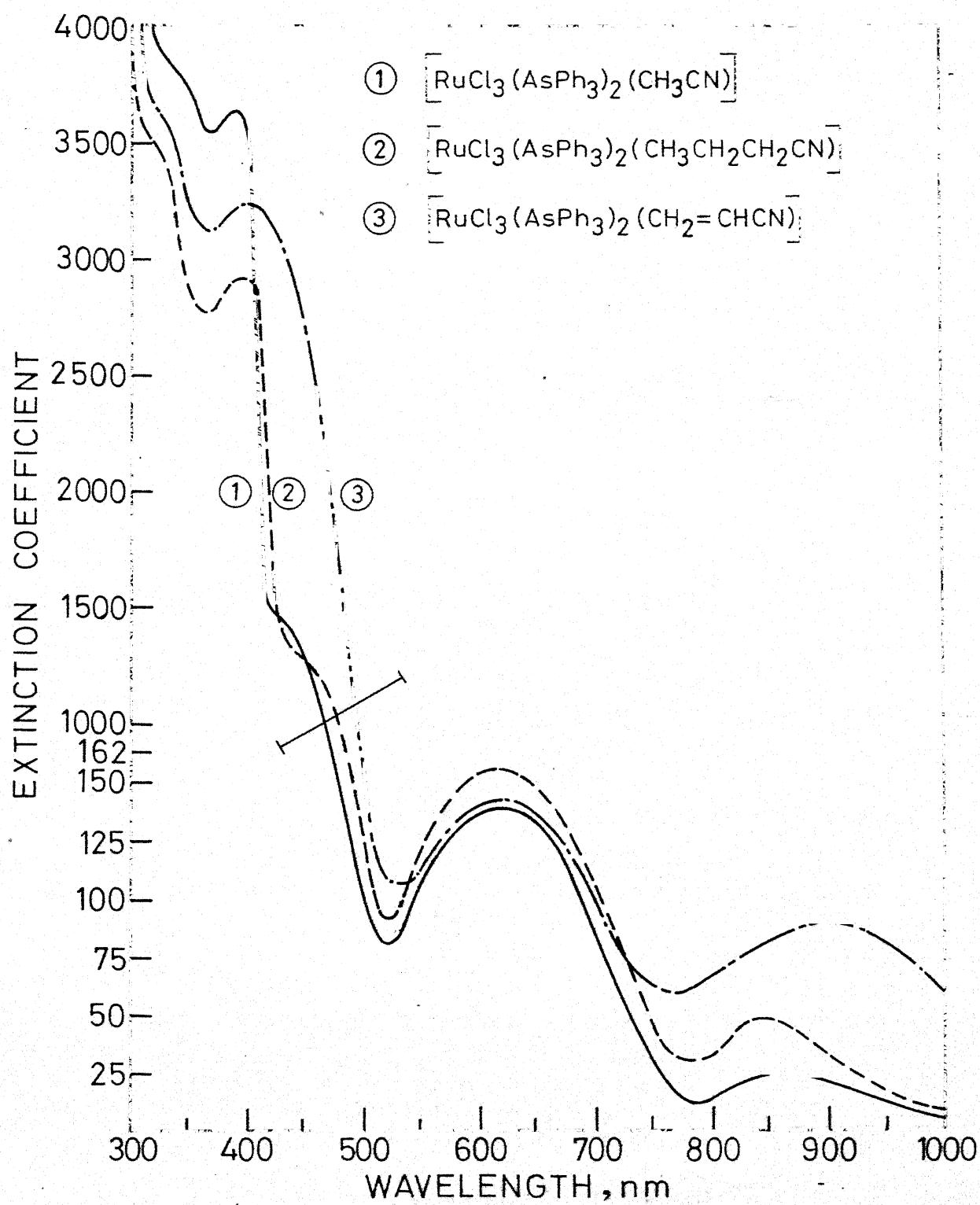
Fig·II.2 ELECTRONIC SPECTRA
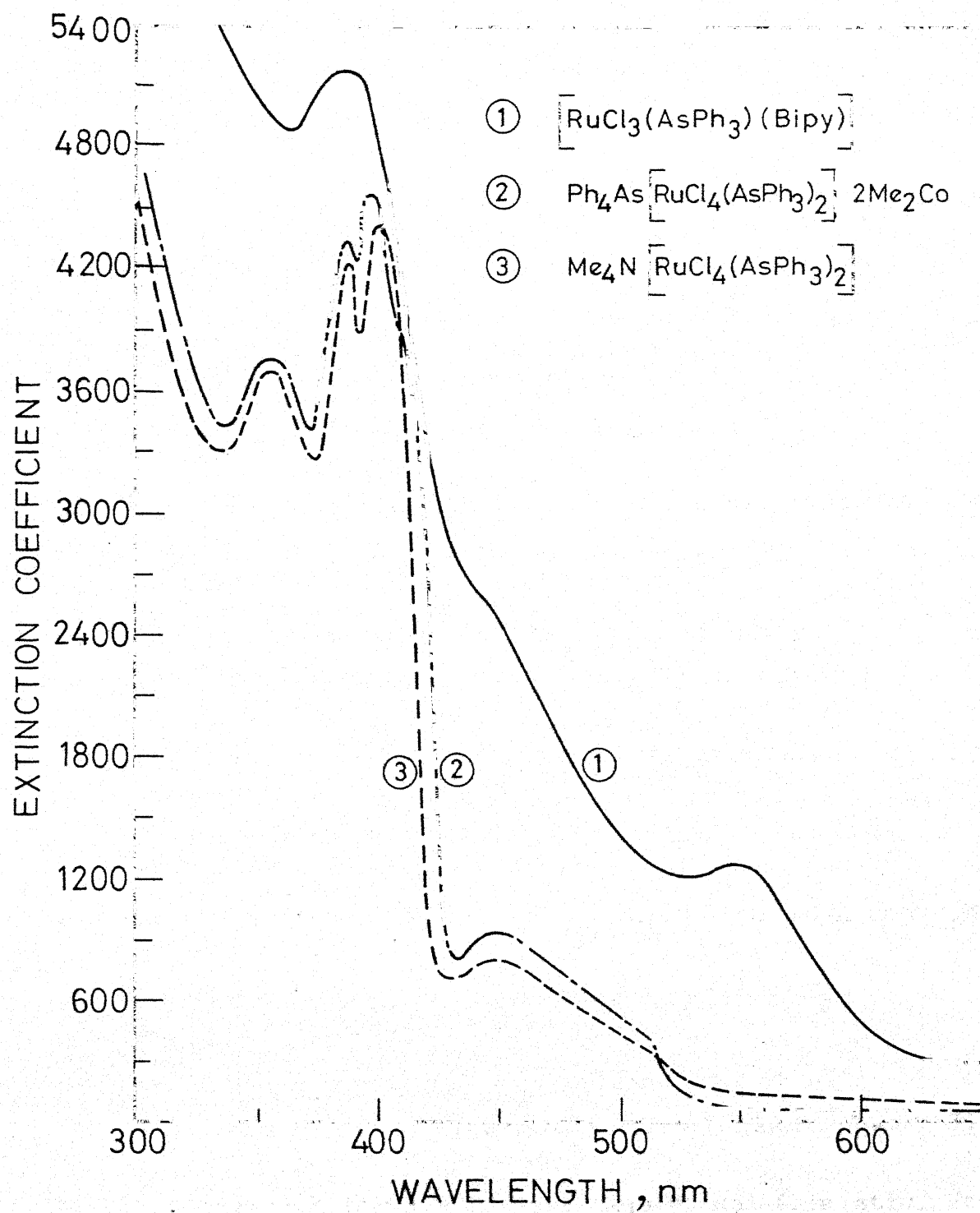
Fig. II.3 ELECTRONIC SPECTRA

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CHAPTER III

RUTHENIUM(III) AND RUTHENIUM(II) COMPLEXES CONTAINING TRIPHENYL-PHOSPHINE OR TRIPHENYLARSINE AND OTHER LIGANDS

Only a few ruthenium(III) complexes with tertiary mono-arsines as one of the ligands have been reported in the litera-ture.[1-4] The study of the reactions of ruthenium(III) and ruthenium(II) complexes of phosphines and arsines with β-di-ketones appears to be a neglected one.[5] Therefore, it is interesting to study the reactions of β-diketones with ruthe-nium(II) phosphine and arsine complexes.

In this chapter the reactions of $[RuCl_3(AsPh_3)_3]$ with ammonia, hydrazines, amine, thiocyanate and carboxylic acids are reported. The reactions of β-diketones (acetylacetone, dibenzoylmethane and benzoylacetone) with $[RuCl_2(PPh_3)_2]_n$ and $[RuCl_2(AsPh_3)_2]_2$ have also been studied and the results,

discussed. Besides, a new ruthenium(III) complex, tribromo-tris(triphenylarsine)ruthenium(III), $[RuBr_3(AsPh_3)_3]$ has also been synthesized. The structures of these complexes have been proposed on the basis of analytical, spectral (ir and visible), magnetic, conductivity, molecular weight and other data.

EXPERIMENTAL

All the chemicals used were of chemically pure or Analar grade.

Trichloro-tris(triphenylarsine)ruthenium(III), dichloro-bis(triphenylphosphine)ruthenium(II) and dichloro-bis(triphenyl-arsine)ruthenium(II) were prepared by the literature methods.[6-8]

PREPARATIONS

(a) Ruthenium(III) Complexes

(i) Di-μ-thiocyanato-bis[dithiocyanato-bis(triphenylarsine)-ruthenium(III)],$[Ru(SCN)_3(AsPh_3)_2]_2$

A solution of 0.4 g of $[RuCl_3(AsPh_3)_3]$ in 10 ml of benzene was added to a solution of 0.8 g of ammonium or potassium thiocyanate in 5 ml of ethanol. The mixture was heated on a water-bath for 5 minutes whereby a dark blue solution was obtained. After evaporating the solvent, the residue was washed with water to remove the excess thiocyanate and ammonium or potassium chloride

formed during the reaction. It was then extracted with dichloromethane. The extract was concentrated to about 5 ml and ether was added to this whereby a bluish-green compound separated out which was filtered, washed with ether and dried under vacuum.

(ii) Di-μ-chloro-bis[carboxylato chloro-bis(triphenylarsine)-ruthenium(III)], $[RuCl_2(AsPh_3)_2(RCOO)]_2$ ($R = CH_3$ or C_2H_5)

0.5 ml of the carboxylic acid (acetic or propionic acid) was added to a saturated solution of 0.2 g of $[RuCl_3(AsPh_3)_3]$ in 5 ml of benzene. The mixed solution was heated on a water-bath for about 10 minutes. On cooling, green crystals of the complex separated out which were filtered, washed with ether and dried under vacuum.

(iii) Tribromo-tris(triphenylarsine)ruthenium(III) $[RuBr_3(AsPh_3)_3]$

A solution of 0.2 g of $RuCl_3.3H_2O$ in methanol (25 ml) was mixed with an aqueous solution of hydrobromic acid (25 ml, 40%). Lithium bromide (0.6 g) was then added to the resulting solution. After heating the mixture under reflux for about an hour, a solution of 1.2 g of triphenylarsine in methanol (20 ml) was added. The mixture was again heated under reflux for another half an hour whereby brown oily mass separated which was separated by decantation, allowed to solidify and ground with mortar and pestle. It was washed several times with methanol and dried under vacuum.

(b) Ruthenium(II) Complexes

(i) Di-μ-chloro-bis[acetylacetonato bis(triphenylphosphine)-
ruthenium(II)], [RuCl(acac)(PPh$_3$)$_2$]$_2$

A solution of 0.2 g of acetylacetone in 5 ml of ethanol
was added to a suspension of [RuCl$_2$(PPh$_3$)$_2$]$_n$ (0.4 g) in benzene
(20 ml). The mixture was heated under reflux for about 3 hr
whereby a greenish solution was obtained. On concentrating it
to 5 ml, green crystalline complex separated out which was fil-
tered, washed successively with ethanol and ether and dried under
vacuum. It was recrystallised from dichloromethane-methanol.

(ii) Di-μ-chloro-bis[dibenzoylmethanato bis(triphenylphosphine)-
ruthenium(II)], [RuCl(dbm)(PPh$_3$)$_2$]$_2$

This complex was prepared by a similar procedure as in
b(i) taking [RuCl$_2$(PPh$_3$)$_2$]$_n$ and dibenzoylmethane. The green
complex obtained was recrystallized from dichloromethane-methanol.

(iii) Di-μ-chloro-bis[benzoylacetonato bis(triphenylphosphine)-
ruthenium(II)], [RuCl(ba)(PPh$_3$)$_2$]$_2$

This complex was prepared using the same procedure as in
b(i) taking [RuCl$_2$(PPh$_3$)$_2$]$_n$ and benzoylacetone. The complex was
recrystallised from dichloromethane-methanol.

(iv) Di-μ-chloro-bis[acetylacetonato bis(triphenylarsine)-

ruthenium(II)] , [RuCl(acac)(AsPh$_3$)$_2$]$_2$

The procedure similar to the one given in b(i) was used to prepare the complex taking [RuCl$_2$(AsPh$_3$)$_2$]$_2$ and acetylacetone. The complex obtained was recrystallized from dichloromethane-methanol.

(v) Di-μ-chloro-bis[dibenzoylmethanato bis(triphenylarsine)-

ruthenium(II)] , [RuCl(dbm)(AsPh$_3$)$_2$]$_2$

This complex was prepared in a similar way as described in b(i) using [RuCl$_2$(AsPh$_3$)$_2$]$_2$ and dibenzoylmethane and recrystallized from dichloromethane and methanol.

(vi) Di-μ-chloro-bis[benzoylacetonato bis(triphenylarsine)-

ruthenium(II)] , [RuCl(ba)(AsPh$_3$)$_2$]$_2$

This complex was also prepared by the similar procedure as in b(i) using [RuCl$_2$(AsPh$_3$)$_2$]$_2$ and benzoylacetone and recrystallized from dichloromethane and methanol.

(vii) [RuCl$_2$(AsPh$_3$)$_2$L$_2$] (L = NH$_3$, CH$_3$NH$_2$, NH$_2$NH$_2$ or C$_6$H$_5$NHNH$_2$)

These complexes were prepared by the following procedure: 0.2 g of the ruthenium(III) complex, [RuCl$_3$(AsPh$_3$)$_3$] was suspended in 10 ml of ethanol. The amine or hydrazine (1 ml) was added to it. The solution was then stirred for about 5 hr whereby rose coloured crystals appeared.

The procedure to prepare the ammonia complex was as follows: Ethanol (10 ml) was first saturated with ammonia gas and the ruthenium complex [$RuCl_3(AsPh_3)_3$] (0.2 g) was suspended in it. On stirring the contents for a few hours, a compound was separated which was filtered, washed with ether and dried under vacuum. Since these complexes showed signs of decomposition when they were dissolved in any solvent, they could not, therefore, be recrystallized.

The analysis for chloride in the complexes was carried out by the standard method.[9] Carbon, hydrogen and nitrogen analyses, melting points, infrared spectra, electronic spectra, magnetic susceptibility and conductivity measurements were obtained according to the methods given in Chapter II. The molecular weights of the compounds were measured cryoscopically using highly purified bromoform as solvent. All the results are given in Table III.1 and Table III.2.

RESULTS AND DISCUSSION

Magnetic Susceptibility

The values of the magnetic moment of all the complexes of ruthenium(III) reported in this chapter lie around 1.9 B.M. (Table III.1) which correspond to paramagnetism equivalent to one unpaired electron in a strong ligand field. All the complexes

Table III.1

Analytical data, colour, melting point and magnetic moment of the complexes

Complex	Colour	M.P. °C	Analysis								Mag. moment B.M.
			Calculated (%)				Found (%)				
			C	H	N	Cl or Br	C	H	N	Cl or Br	
1	2	3	4	5	6	7	8	9	10	11	12
$Ru(SCN)_3(AsPh_3)_2$	Bluish green	135	52.77	3.38	4.74		52.31	3.62	4.44		1.8
$RuCl_2(AsPh_3)_2(CH_3COO)$	Green	169	54.12	3.92	—	Cl,8.41	53.96	4.02	—	Cl,8.62	1.9
$RuCl_2(AsPh_3)_2(CH_3CH_2COO)$	"	161	54.62	4.08	—	Cl,8.27	54.22	4.18	—	Cl,8.16	1.9
$RuBr_3(AsPh_3)_3$	Brown	144-45	51.47	3.57	—	Br,19.06	51.09	3.58	—	Br,19.66	1.92
$RuCl(acac)(AsPh_3)_2$	Green	265	57.45	4.42	—	Cl,4.24	56.98	3.99	—	Cl,4.36	D
$RuCl(dbm)(AsPh_3)_2$	"	285	63.01	4.22	—	Cl,3.65	62.70	4.60	—	Cl,3.42	D
$RuCl(ba)(AsPh_3)_2$	"	249	60.68	4.19	—	Cl,3.89	61.01	4.20	—	Cl,4.01	D
$RuCl(acac)(PPh_3)_2$	"	215	62.44	4.81	—	Cl,4.61	62.11	4.96	—	Cl,4.89	D
$RuCl(dbm)(PPh_3)_2$	"	234	67.9	4.54	—	Cl,3.93	67.53	4.69	—	Cl,4.31	D
$RuCl(ba)(PPh_3)_2$	"	216	65.73	4.64	—	Cl,4.22	65.97	4.81	—	Cl,4.01	D
$RuCl_2(AsPh_3)_2(NH_3)_2$	Rose	147	52.83	4.40	3.42	Cl,8.67	52.43	4.32	3.30	Cl,8.72	D
$RuCl_2(AsPh_3)_2(CH_3NH_2)_2$	"	203	53.96	4.73	3.31	Cl,8.39	54.29	4.79	3.40	Cl,8.62	D

Table III.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12
$RuCl_2(AsPh_3)_2(NH_2NH_2)_2$	Rose	159	50.95	4.48	6.6	Cl,8.36	51.38	4.55	5.97	Cl,8.16	D
$RuCl_2(AsPh_3)_2(C_6H_5NHNH_2)_2$	"	133	57.61	4.60	5.60	Cl,7.09	57.68	4.80	5.20	Cl,7.31	D

acac, acetylacetonate; dbm, dibenzoylmethanate;

ba, benzoylacetonate; D, diamagnetic.

of ruthenium(II) are diamagnetic as are other octahedral comp-
lexes of ruthenium(II).

Electronic Spectra

The ground state of ruthenium(II) in an octahedral field
(t_{2g}^6 configuration) is $^1A_{1g}$ which conform with the results of
the magnetic moment value. The excited states corresponding to
$t_{2g}^5 e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ in increasing
order of energy. Thus, one should expect four transitions,
$^1A_{1g} > ^3T_{1g}$; $^1A_{1g} -> ^3T_{2g}$; $^1A_{1g} > ^1T_{1g}$ and $^1A_{1g} \cdot > ^1T_{2g}$.
The low spin d^6 system is less complicated so far as charge
transfer excited states are concerned because no states from
$L \to M$ transition are possible at low energies.[10,11] In the
electronic spectra of ruthenium(II) complexes, three bands in
some cases and four or five bands in other cases appear in the
visible region. The positions of these bands and the respective
assignments are given in Table III.2. From the band positions,
the values of 10Dq, B, β and C have been calculated.[10] Values
are within the range of those found for other octahedral ruthe-
nium(II) complexes which justify the assignments. The values of
the molar extinction coefficients for the bands in the range of
400-500 nm were found to be more than those of the usual d-d
transition. This may be due to the mixing of the energy levels
with those corresponding to the neighbouring intense charge trans-
fer bands around 390 nm. Tentatively one may justify this

Table III.2

Electronic spectral data of the complexes[a]

| Complex | Band position | | ε | Assignment | 10 Dq cm^{-1} | B cm^{-1} | C cm^{-1} | β |
	λ_{nm}	cm^{-1}						
1	2	3	4	5	6	7	8	9
Ru(SCN)$_3$(AsPh$_3$)$_2$	623	16,051	260	$^2T_{2g} \longrightarrow {}^2A_{2g}$				
	385	25,974	3,349	Charge Transfer				
RuCl$_2$(AsPh$_3$)$_2$(CH$_3$COO)	900	11,111	323	—				
	520	19,230	820	$^2T_{2g} \longrightarrow {}^2A_{2g}$				
	400	25,000	2,152	Charge Transfer				
RuCl$_2$(AsPh$_3$)$_2$(CH$_3$COO)^c	590	16,950	—	$^2T_{2g} \longrightarrow {}^2A_{2g}$				
	440	22,727	—	Charge Transfer				
RuCl$_2$(AsPh$_3$)$_2$(CH$_3$CH$_2$COO)	900	11,111	208	—				
	535	18,691	630	$^2T_{2g} \longrightarrow {}^2A_{2g}$				
	410	24,390	1,817	Charge Transfer				
	350	28,571	2,930					

a, in chloroform solution except where indicated; c, Nujol mull; b, broad

Table III.2. (contd.)

1	2	3	4	5	6	7	8	9
RuBr$_3$(AsPh$_3$)$_3$	940	10,638	390	—				
	520	19,230	1,453	$^2T_{2g} \longrightarrow {}^2A_{2g}$				
	430	23,255	2,860	Charge Transfer				
RuCl(acac)(AsPh$_3$)$_2$	590	16,950	392	$^1A_{1g} \longrightarrow {}^1T_{1g}$	19,400	444	2,400	0.7
	420	23,805	2,567	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390	25,640	5,133	Charge Transfer				
RuCl(dbm)(AsPh$_3$)$_2$	590	16,950	418	$^1A_{1g} \longrightarrow {}^1T_{1g}$	19,400	360	2,400	0.58
	440	22,727	5,072	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390	25,640	10,550	Charge Transfer				
RuCl(ba)(AsPh$_3$)$_2$	590	16,950	351	$^1A_{1g} \longrightarrow {}^1T_{1g}$	19,400	462	2,400	0.74
	405	24,691	5,777	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390	25,640	7,216	Charge Transfer				
RuCl(acac)(PPh$_3$)$_2$	610	16,393	256	$^1A_{1g} \longrightarrow {}^1T_{1g}$	18,800	465	2,400	0.74
	430	23,255	2,224	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390	25,640	2,816	Charge Transfer				

Table III.2 (contd.)

1	2	3	4	5	6	7	8	9
$RuCl(dbm)(PPh_3)_2$	640	15,625	238	$^1A_{1g} \longrightarrow {}^1T_{1g}$	18,025	382	2,400	0.61
	460	21,740	3,181	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	400	25,000	9,806	Charge Transfer				
$RuCl(ba)(PPh_3)_2$	860	11,600	325	$^1A_{1g} \longrightarrow {}^3T_{1g}$				
	610	16,393	400	$^1A_{1g} \longrightarrow {}^1T_{1g}$				
	420	23,800	2,411	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390	25,640	6,751	Charge Transfer				
$RuCl_2(AsPh_3)_2(CH_3NH_2)_2{}^c$	650	15,384	—	$^1A_{1g} \longrightarrow {}^3T_{1g}$				
	420(b)	23,810	—	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390(sh)	25640	—	Charge Transfer				
$RuCl_2(AsPh_3)_2(C_6H_5NHNH_2)_2{}^c$	550(b)	18,182	—	$^1A_{1g} \longrightarrow {}^1T_{1g}$				
	475(b)	21,053	—	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	370(sh)	27,027	—	Charge Transfer				
$RuCl_2(AsPh_3)_2(NH_2NH_2)_2{}^c$	640	15,625	—	$^1A_{1g} \longrightarrow {}^3T_{1g}$	22,190	240	2,187	0.4
	500	20,000	—	$^1A_{1g} \longrightarrow {}^1T_{1g}$				
	420	23,810	—	$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	390	25,640	—	Charge Transfer				

statement by the fact that as the energy difference between 390 nm band and the other bands increases, the values of the extinction coefficient decrease because of the decrease in the mixing of the energy levels.

The ground state of ruthenium(III) (t_{2g}^5 configuration) is $^2T_{2g}$ and the first excited doublet levels in order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which arise from $t_{2g}^4 e_g^1$ configuration.[12] In most of the ruthenium(III) complexes the uv and visible spectra show only charge transfer bands.[10] Thus the band or bands in the 400 nm region are assigned to charge transfer transition. However, the extinction coefficients of the band in 600 nm region in all the ruthenium(III) complexes are rather low as compared to those which one should expect for the charge transfer bands. It is, therefore, assigned to $^2T_{2g} \rightarrow {}^2A_{2g}$ transition corresponding to the energy change of 10Dq - 3B - C. The position of the bands in this region is also in conformity with that of the bands in other octahedral ruthenium(III) complexes.[13]

In the complexes containing carboxylate anion as a ligand, a weak band is found in the spectra around 900 nm region. This may be due to the pentacoordinate species formed in solution as a result of dissociation of the complex. In order to justify this, the spectra of the complexes were repeated in solution containing varying amounts of carboxylate anion concentration. It was found that as the concentration of the carboxylate anion

increased, the intensity of 900 nm band decreased and finally

in a solution containing 0.35 mole of carboxylate anion the band

completely disappeared (Fig. III.1). When the spectra were

repeated in Nujol mull no band in the 900 nm region was detec-

ted in any of the carboxylate complexes. These observations

led us to conclude that as the carboxylate complexes were disso-

lved in the solvent, there was an equilibrium between penta- and

hexa-coordinated species with the dissociation of $RCOO^-$ group.

$$[RuCl_2(AsPh_3)_2(RCOO)]_2 \rightleftharpoons [RuCl_2(AsPh_3)_2]_2^{2+} + 2 RCOO^-$$
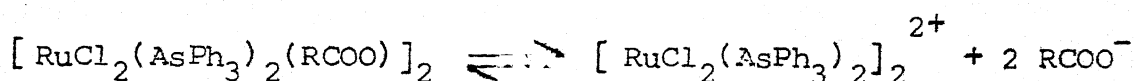
These conclusions are in conformity with the earlier observa-

tions in other ruthenium(III) complexes discussed in Chapter II

of the thesis.

In the spectrum of $[RuBr_3(AsPh_3)_3]$ in chloroform solution

there appeared three bands at 940, 520 and 430 nm. The presence

of the band at 940 nm suggested the presence of pentacoordinated

species in solution. In order to confirm this, the following

experiments were performed.

(i) The spectrum of the complex was taken in Nujol mull

which showed three bands at 940, 520 and 430 nm. This suggested

the presence of pentacoordinated species in the solid state as

well.

(ii) A number of solutions of the complex were prepared in

chloroform to which varying amounts of triphenylarsine were added

and the spectra of these solutions were taken. In every case the same three bands at 940, 520 and 430 nm appeared indicating the presence of five coordinated species in solution.

(iii) A number of solutions of the complex were prepared in chloroform to which varying amounts of lithium bromide solution in methanol was added. In every case the band at 940 nm disappeared and a new band at 625 nm appeared besides the bands at 520 and 430 nm (Fig. III.1).

All these observations could be explained if one assumes the following equilibrium:

$[RuBr_2(AsPh_3)_3]Br$ Solvent containing AsPh₃ $[RuBr_2(AsPh_3)_3]^+ \ Br^-$
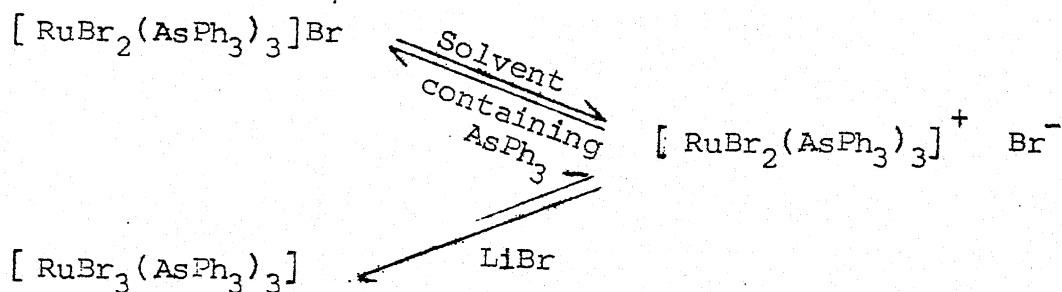
$[RuBr_3(AsPh_3)_3]$ LiBr

$[RuBr_2(AsPh_3)_3]Br$ is thus assumed to be the predominant species present in the solid state.

The conductivity of the compound $[RuBr_3(AsPh_3)_3]$ in nitrobenzene was found to be $\approx 8 \ ohm^{-1}cm^2mol^{-1}$ (expected value in nitrobenzene for the species $[RuBr_2(AsPh_3)_3]^+ \ Br^-$ is 20-30 $ohm^{-1}cm^2mol^{-1}$). The relatively lower value may be due to the partial dissociation of the complex, thereby lowering the effective

concentration of the ionic species in solution. Another int<

resting aspect regarding the compound is that its behaviour :

not similar to $[RuCl_3(AsPh_3)_3]$ in many reactions[13] which als<

indicated the presence of different type of species in solutio

Infrared Spectra

(i) Thiocyanate complex

The ir spectrum of the thiocyanate complex showed bands

at 2140, 2080 and 790 cm^{-1} besides the characteristic bands of

triphenylarsine. The presence of two bands in 2100 cm^{-1} region

suggested that SCN groups are linked in the complex, possibly,

in two different ways. The band at 2080 cm^{-1} may be assigned to

$\nu_{(CN)}$ of the N-bonded terminal thiocyanato group while the band

at 2140 cm^{-1} to the $\nu_{(CN)}$ arising from the bridged SCN group.[14,15]

The band at 790 cm^{-1} is assigned to the skeletal mode having major

contribution from $\nu_{(CS)}$ of the thiocyanato group. The positions

of the bands at 790 and 2080 cm^{-1} suggest that the bonding is

through nitrogen atom of the NCS group.[16,17] This is what one

should expect in the spectrum of the complex if it has two strongly

π-acceptor ligands (viz.., $AsPh_3$) attached to the same metal ion

where SCN group is also linked.[18,19] Thus, one could suggest on

the spectral (ir and visible) and magnetic studies, the following

tentative structure of the complex:
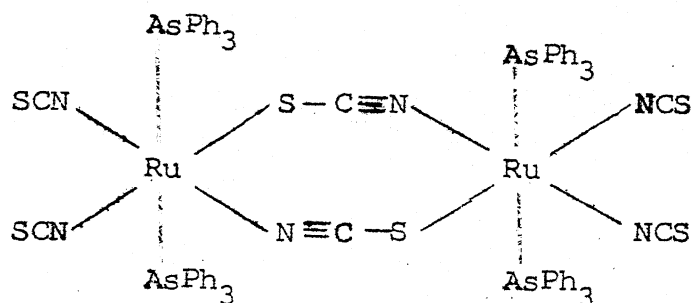
The dimeric nature of the suggested structure was further con-
firmed by the value of its molecular weight, (experimental value
1760 and the calculated for the dimer, 1774).

(ii) Carboxylate complexes

The ir spectra of the carboxylato complexes showed bands
in the region 1660 and 1605 cm^{-1}. These may be assigned to the
characteristic bands of carboxylate group behaving as unidentate.
The bands in the region 1590-1650 cm^{-1} are considered diagnostic
of unidentate coordination.[20] These compounds are soluble in
chloroform and dichloromethane. In most of the solvents the
complexes are partially dissociated as suggested by the molecular
weights determined cryoscopically (eratic values which suggest
minimum of two different species in solution) and by the visible
spectral studies. Thus, the following tentative octahedral
structures have been proposed for these complexes on the basis
of the spectral and magnetic studies:

$R = CH_3$ or CH_3CH_2
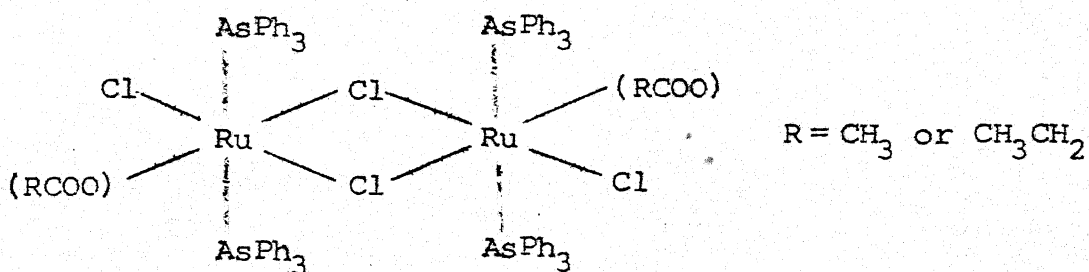
(iii) β-Diketone complexes of ruthenium(II)

Two or three sharp bands appeared in the region 1530 cm^{-1} to 1610 cm^{-1} (Table III.3) in the spectra of all the β-diketone complexes. The positions of these bands are characteristic of the mixed mode of vibrations arising due to the normal coordinate having contributions from $\nu_{(C=O)}$ and $\nu_{(C=C)}$ of the coordinated β-diketones.[21] All the characteristic bands due to triphenylphosphine or arsine and β-diketones were also present in the spectra. Due to limited solubility in bromoform, attempts to measure the molecular weights of these compounds were not successful. However, the values obtained from these measurements were found to be nearer to those of the values calculated for dimer. Hence dimer structures have been assumed. In case the arrangement of the ligand molecules has to be octahedral as indicated by spectral (visible) and magnetic studies, the compounds have to be dimers with chlorobridges. Thus, on the basis of these, the following bridged structure is proposed for all these complexes:
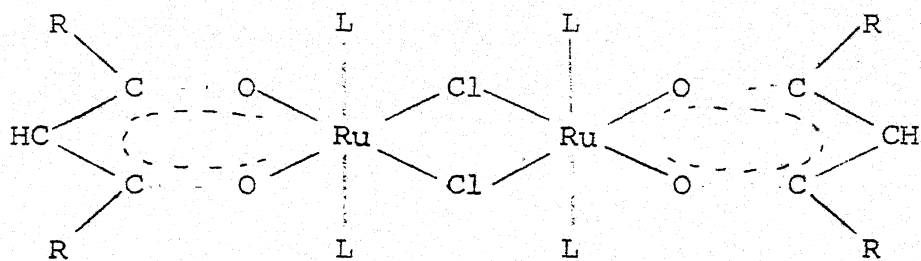
L = PPh$_3$ or AsPh$_3$

R = C$_6$H$_5$, CH$_3$ and/or CH$_3$, C$_6$H$_5$

(iv) Amine complexes of ruthenium(II)

The ir spectrum of the ammonia complex $[RuCl_2(AsPh_3)_2(NH_3)_2]$ showed bands at 3400, 3360, 3270, 3200, 1620 and 1245 cm^{-1}. The bands which appeared in the range 3400-3000 cm^{-1} have been assigned to $\nu_{(NH)}$ of NH_3. The band at 1620 cm^{-1} may be due to $\delta_d(NH_3)$ and the band at 1245 cm^{-1} due to $\delta_s(NH_3)$.[21] The ir spectrum of $[RuCl_2(AsPh_3)_2(CH_3NH_2)_2]$ showed bands at 3360 and 3280 cm^{-1}. The spectra of primary amines show two bands due to $\nu_{(NH)}$ in the region 3500-3300 cm^{-1}.[22] So the bands at 3360 and 3280 cm^{-1} may be attributed to $\nu_{(NH)}$ of the coordinated methyl-amine group. These complexes are air sensitive and change to a black compound when kept in air for sometime.

In the complexes of the type $[RuCl_2(AsPh_3)_2L_2]$ ($L = H_2NNH_2$ or $C_6H_5NHNH_2$), the hydrazine or phenylhydrazine should act as monodentate if an octahedral arrangement of the ligand molecule is assumed around the metal ion as indicated by visible and magnetic studies. In general hydrazine acts as bidentate in its complexes but the nitrogen elemental analysis clearly indicated the presence of two hydrazine molecules in the complex. The ir spectrum of the hydrazine complex showed bands at 3370 and 3330 cm^{-1} and that of the phenylhydrazine complex, at 3300 and 3270 cm^{-1}. These bands are assigned to $\nu_{(NH)}$. The following octahedral structure has been proposed for these complexes:

Table III.3

Some important infrared frequencies of the complexes

Complex	Frequency in cm^{-1}
$RuCl(acac)(AsPh_3)_2$	1565(m) and 1530(s)
$RuCl(dbm)(AsPh_3)_2$	1600(m) and 1530(s)
$RuCl(ba)(AsPh_3)_2$	1560(m) and 1530(s)
$RuCl(acac)(PPh_3)_2$	1570(m) and 1535(s)
$RuCl(dbm)(PPh_3)_2$	1595(m) and 1530(s)
$RuCl(ba)(PPh_3)_2$	1610(m), 1570(s) and 1530(s)
$RuCl_2(AsPh_3)_2(NH_3)_2$ *	3400, 3360, 3270, 3200, 1620 and 1245
$RuCl_2(AsPh_3)_2(CH_3NH_2)_2$ *	3360 and 3280
$RuCl_2(AsPh_3)_2(NH_2NH_2)_2$ *	3370 and 3330
$RuCl_2(AsPh_3)_2(C_6H_5NHNH_2)_2$ *	3300, 3270 and 1630

m = medium;   s = strong;

*all the bands are of medium intensity.

AsPh$_3$

L ⟍ ⟋Cl

Ru

Cl⟋ ⟍L

AsPh$_3$
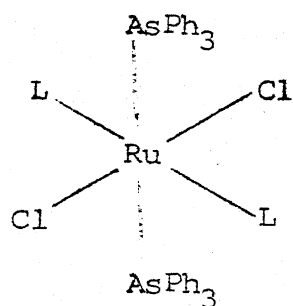
L = NH$_3$ or CH$_3$NH$_2$ or
hydrazine or phenyl-
hydrazine.

One of the interesting properties of these compounds is that
they decompose when dissolved in solvents like chloroform or
dichloromethane.
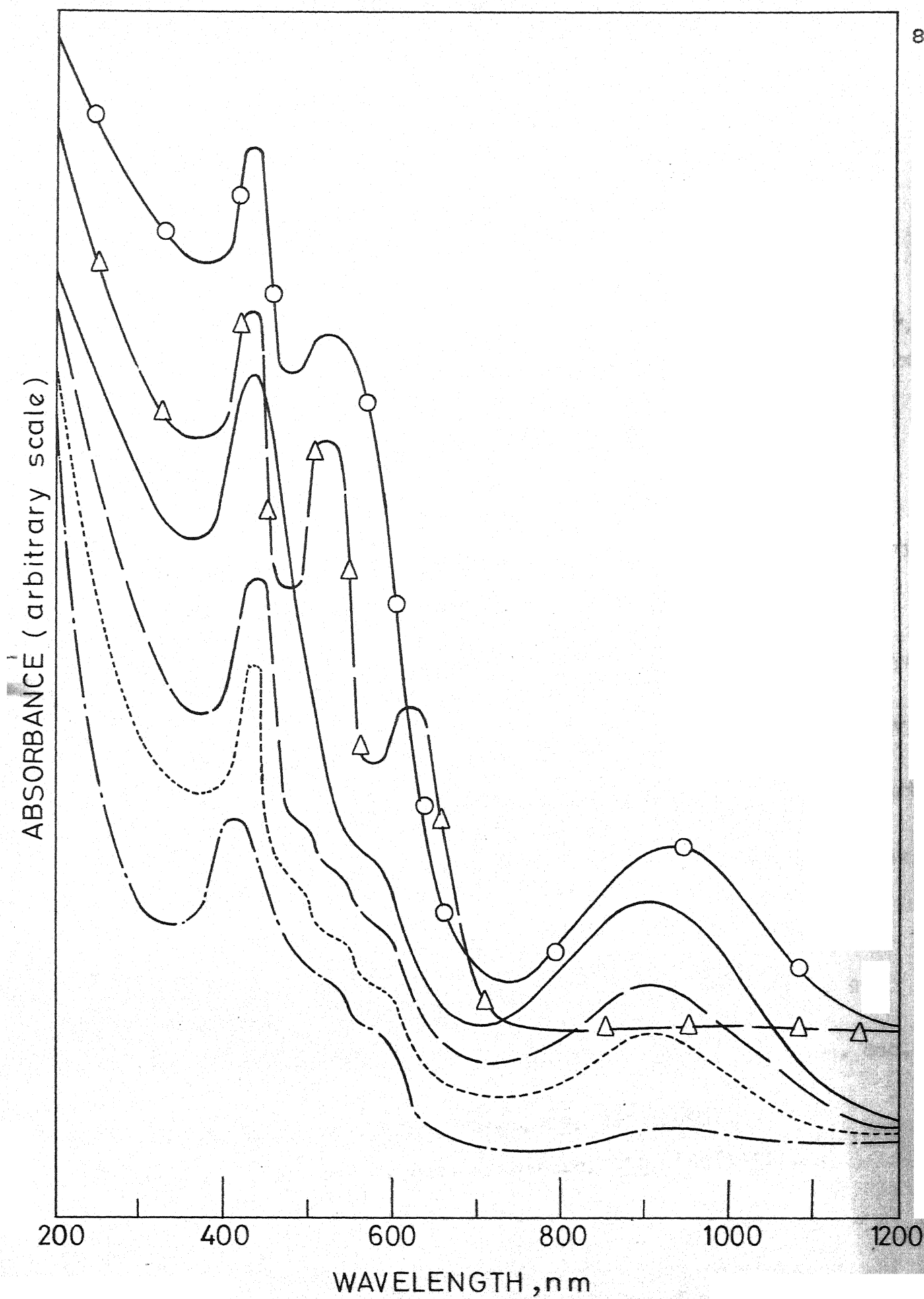
Fig. III .1 ELECTRONIC SPECTRA

Fig. III.1: (a) Electronic spectrum of (i) $RuCl_2(AsPh_3)_2(CH_3COO)$
in chloroform (-   ), (ii) $RuCl_2(AsPh_3)_2(CH_3COO)$
in chloroform with 0.017 M CH_3COOH (━ ━ ━ ━ ━ ━),(iii)
$RuCl_2(AsPh_3)_2(CH_3COO)$ in chloroform with 0.35 M
CH_3COOH taken immediately after adding CH_3COOH(-----),
(iv) $RuCl_2(AsPh_3)_2(CH_3COO)$ in chloroform with 0.35 M
CH_3COOH, taken after 30 min. of mixing (—·—·—·—)
and (b) electronic spectrum of (i) $RuBr_3(AsPh_3)_3$ in
chloroform (· —O— ·O ·—O——) and (ii) $RuBr_3(AsPh_3)_3$
in chloroform to which LiBr in methanol was added
(—Δ— Δ—·Δ—).

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CHAPTER   IV

β-DIKETONATO(TRIPHENYLPHOSPHINE)-
AND (TRIPHENYLARSINE) COMPLEXES
OF RUTHENIUM(III)

Carboxylic acids and their platinum-metal derivatives
feature extensively as homogeneous catalysis.[1-5] A large number
of carboxylato(triphenylphosphine) complexes of ruthenium(II)
have been reported.[6] Only a very little amount of work has
been done as far as β-diketonato(triphenylphosphine) deriva-
tives of ruthenium(II) are concerned.[7] Similar such work on
ruthenium(III) seems to be a neglected one. In this chapter
the reactions of β-diketones with ruthenium(III) triphenylphos-
phine and triphenylarsine complexes are described.

EXPERIMENTAL

All the reagents used were of chemically pure or Analar grade.

Trichloro-tris(triphenylarsine)ruthenium(III), tribromo-tris(triphenylarsine)ruthenium(III), trichloro-tris(triphenylphosphine)ruthenium(III) and tribromo-bis(triphenylphosphine)-(methanol)ruthenium(III) were prepared according to the literature methods.[8-11]

PREPARATION OF COMPLEXES

(i) Acetylacetonato dichloro-bis(triphenylarsine)ruthenium(III), [$RuCl_2(acac)(AsPh_3)_2$]

[$RuCl_3(AsPh_3)_3$] (0.25 g) was dissolved in benzene (10 ml) and a solution of acetylacetone (0.5 ml) in ethanol (5 ml) was added to it. The mixture was heated under reflux for 3 hr whereby a green solution was obtained. The solution was concentrated to about 5 ml on a water-bath and then cooled. Green crystals appeared. These were filtered and washed successively with benzene and ether. The crystals were recrystallized from dichloromethane and methanol mixture and dried under vacuum.

(ii) Dichloro dibenzoylmethanato-bis(triphenylarsine)-ruthenium(III), [$RuCl_2(dbm)(AsPh_3)_2$]

This complex was prepared in a similar way as in (i) taking [$RuCl_3(AsPh_3)_3$] and dibenzoylmethane. The green

complex obtained was recrystallized from dichloromethane-methanol.

(iii) Benzoylacetonato dichloro-bis(triphenylarsine)ruthenium(III), [RuCl$_2$(ba)(AsPh$_3$)$_2$]

This complex was prepared by a similar procedure as in (i) taking [RuCl$_3$(AsPh$_3$)$_3$] and benzoylacetone. The green complex thus formed was recrystallized from dichloromethane-methanol.

(iv) Acetylacetonato dichloro-bis(triphenylphosphine)ruthenium(III), [RuCl$_2$(acac)(PPh$_3$)$_2$]

[RuCl$_3$(PPh$_3$)$_3$] (0.25 g) was dissolved in 10 ml of benzene and a solution of acetylacetone (0.5 ml) in ethanol (5 ml) was added to it. The mixture after heating under reflux for 3 hr, was concentrated to about 5 ml on a water-bath and cooled. Green crystals of the complex were formed which were filtered, washed with benzene and ether and dried under vacuum. Recrystallized from dichloromethane-methanol to yield green crystals of the complex.

(v) Dichloro dibenzoylmethanato-bis(triphenylphosphine)-ruthenium(III), [RuCl$_2$(dbm)(PPh$_3$)$_2$]

This complex was prepared in a similar manner as in (iv) taking [RuCl$_3$(PPh$_3$)$_3$] and dibenzoylmethane. The complex

obtained was recrystallized from dichloromethane-methanol.

(vi) Benzoylacetonato dichloro-bis(triphenylphosphine)-ruthenium(III), $[RuCl_2(ba)(PPh_3)_2]$

This complex was prepared by a similar procedure as in (iv) by taking $[RuCl_3(PPh_3)_3]$ and benzoylacetone. The complex obtained was recrystallized from dichloromethane-methanol.

(vii) Acetylacetonato dibromo-bis(triphenylarsine)ruthenium(III), $[RuBr_2(acac)(AsPh_3)_2]$

The mixed solution of $[RuBr_3(AsPh_3)_3]$ (0.25 g) in benzene (10 ml) and acetylacetone (0·5 ml) in ethanol (5 ml) was heated under reflux for 3 hr. The resulting solution after concentrating on a water-bath to about 5 ml was cooled whereby brown crystals of the complex obtained. These crystals were filtered, washed with benzene and ether and dried under vacuum. Recrystallized from dichloromethane-methanol.

(viii) Dibromo dibenzoylmethanato-bis(triphenylarsine)ruthenium(III), $[RuBr_2(dbm)(AsPh_3)_2]$

This complex was prepared by the same method as in (vii) taking $[RuBr_3(AsPh_3)_3]$ and dibenzoylmethane. The brown complex obtained was recrystallized from dichloromethane-methanol.

(ix) Benzoylacetonato dibromo-bis(triphenylarsine)ruthenium(III),
[RuBr$_2$(ba)(AsPh$_3$)$_2$]

This complex was prepared in the same way as in (vii) by using [RuBr$_3$(AsPh$_3$)$_3$] and benzoylacetone. The complex was recrystallized from dichloromethane-methanol.

(x) Acetylacetonato dibromo-bis(triphenylphosphine)ruthenium(III),
[RuBr$_2$(acac)(PPh$_3$)$_2$]

A solution of [RuBr$_3$(PPh$_3$)$_2$.MeOH] (0.25 g) in benzene (10 ml) and acetylacetone (0.5 ml) in alcohol (5 ml) was heated under reflux for 3 hr. The solution was then concentrated on a water-bath to about 5 ml and cooled whereby brown crystals of the complex were separated. They were filtered and washed with benzene and ether and dried under vacuum. They were then recrystallised from dichloromethane-methanol.

(xi) Dibromo dibenzoylmethanato-bis(triphenylphosphine)ruthenium(III), [RuBr$_2$(dbm)(PPh$_3$)$_2$]

This complex was prepared in a similar manner as in (x) by using[RuBr$_3$(PPh$_3$)$_2$.MeOH]and dibenzoylmethane. The complex was recrystallised from dichloromethane-methanol.

(xii) Benzoylacetonato dibromo-bis(triphenylphosphine)ruthenium(III), [RuBr$_2$(ba)(PPh$_3$)$_2$]

This complex was also prepared by the same method as described in (x) by taking [RuBr$_3$(PPh$_3$)$_2$.MeOH]and benzoyl-

acetone and recrystallised from dichloromethane and methanol.

Carbon and hydrogen analyses, melting points, infrared spectra, electronic spectra and magnetic susceptibilities were obtained according to the methods given in Chapter II. The chloride and bromide analyses were carried out by the standard methods.[12]

The molecular weights of the complexes were determined cryoscopically (depression in freezing point) using highly purified bromoform. Electron spin resonance spectra of the powdered samples and in chloroform solution were recorded with Varian Associates Model V4502 EPR Spectrophotometer using rectangular cavity in TE_{102} mode and the results are given in Table IV.4.

RESULTS AND DISCUSSION

Elemental analyses and molecular weights of the complexes confirm that these complexes are monomeric with the general formula $[RuX_2(bdk)L_2]$ (X = Cl, Br; bdk = β-diketonate; L = PPh$_3$, AsPh$_3$).

The infrared spectra of the complexes showed all the bands due to triphenylphosphine or triphenylarsine. Besides these, two or three bands were present in the region 1525-1610 cm^{-1}. These may be assigned to the characteristic bands of the coordinated β-diketones arising due to the normal coordinates

Table IV.1

Analytical data, colour, melting point and magnetic moment of the complexes

| Complex | Colour | M.P. °C | ANALYSIS | | | | | | Magnetic moment B.M. |
| | | | Calculated (%) | | | Found (%) | | | |
			C	H	Cl or Br	C	H	Cl or Br	
RuCl$_2$(acac)(AsPh$_3$)$_2$	Green	267	55.72	4.19	8.04	56.12	4.13	7.99	2.54
RuCl$_2$(dbm)(AsPh$_3$)$_2$	"	281	60.77	4.07	7.05	61.28	3.99	7.29	2.53
RuCl$_2$(ba)(AsPh$_3$)$_2$	"	255	58.41	4.13	.7.51	58.98	4.33	7.82	2.10
RuCl$_2$(acac)(PPh$_3$)$_2$	"	215	61.89	4.65	8.93	61.55	4.71	8.69	2.00
RuCl$_2$(dbm)(PPh$_3$)$_2$	"	230	66.59	4.46	7.73	66.41	4.52	7.91	2.71
RuCl$_2$(ba)(PPh$_3$)$_2$	"	214	64.41	4.55	.8.28	64.32	4.44	8.18	2.31
RuBr$_2$(acac)(AsPh$_3$)$_2$	Brown	290	50.62	3.81	16.46	50.45	3.93	16.81	2.03
RuBr$_2$(dbm)(AsPh$_3$)$_2$	"	267	55.84	3.74	14.60	56.03	3.55	14.71	2.07
RuBr$_2$(ba)(AsPh$_3$)$_2$	"	231-33	53.38	3.77	15.47	53.63	3.81	15.41	2.02
RuBr$_2$(acac)(PPh$_3$)$_2$	"	224	55.66	4.19	18.10	55.41	4.07	18.23	1.80
RuBr$_2$(dbm)(PPh$_3$)$_2$	"	222	60.71	4.07	15.87	60.41	4.32	15.99	2.00
RuBr$_2$(ba)(PPh$_3$)$_2$	"	206	58.35	4.12	16.91	58.91	4.57	17.38	1.91

Table IV.2

Some important infrared frequencies and
molecular weight of the complexes

Sl. No.	Complex	Characteristic frequencies of β-diketone cm^{-1}	Molecular weight	
			Calcd	Found
1.	$RuCl_2(acac)(AsPh_3)_2$	1530, 1565	883	842
2.	$RuCl_2(dbm)(AsPh_3)_2$	1540, 1610	1007	988
3.	$RuCl_2(ba)(AsPh_3)_2$	1530, 1570, 1610	945	960
4.	$RuCl_2(acac)(PPh_3)_2$	1530, 1570	795	774
5.	$RuCl_2(dbm)(PPh_3)_2$	1525, 1540, 1600	919	906
6.	$RuCl_2(ba)(PPh_3)_2$	1540, 1560	857	873
7.	$RuBr_2(acac)(AsPh_3)_2$	1530, 1570	972	986
8.	$RuBr_2(dbm)(AsPh_3)_2$	1530, 1570	1096	1120
9.	$RuBr_2(ba)(AsPh_3)_2$	1530, 1570, 1605	1034	1032
10.	$RuBr_2(acac)(PPh_3)_2$	1545, 1575	884	869
11.	$RuBr_2(dbm)(PPh_3)_2$	1535, 1550, 1610	1008	1029
12.	$RuBr_2(ba)(PPh_3)_2$	1535, 1560, 1600	946	932

having contribution from $\nu_{(C=O)}$ and $\nu_{(C=C)}$.[13] In the spectra of the chloro-complexes, the bands assigned to $\nu_{(Ru-Cl)}$ were present around 305 cm^{-1}. The absence of the bands around 280 cm^{-1} in the chloro-complexes indicate that chlorine atom is not acting as a bridging ligand between two ruthenium atoms.[14]

Magnetic Susceptibility

The values of the magnetic moment of all the complexes correspond to one unpaired electron suggesting fully spin paired configuration for the ruthenium ion in +3 oxidation state. However, the magnetic moments of four complexes range from 2.31 to 2.71 B.M. For octahedral ruthenium(III) complexes the maximum value of the magnetic moment theoretically possible is about 2.30 B.M.[15] The values obtained (2.31-2.71 B.M.) neither conform with the expected magnetic moments for fully spin paired configuration nor with those expected for the spin free case (≃ 5.9 B.M.). Further, if the symmetry of the complex is lowered from O_h towards D_{4h} or C_{3v}, the ground state of ruthenium-(III) will be orbitally nondegenerate and the orbital contribution to the magnetic moment will approach to zero. As a result the values of the magnetic moment will be lowered further and approach towards the spin only value (1.73 B.M.).[15] However, if one considers in a complex that the field strength due to ligands and symmetries are close to the spin transition region, small changes in these conditions will then be enough to make

the ground state of the ruthenium(III) ion, a doublet state, a sextet state or a quartet state[16] or these states will be close enough so as to be approachable through thermal energy. With the result, the values of the magnetic moments will be higher than the spin only value depending upon the relative population of the ground and the next excited state (measurement of magnetic susceptibility involves taking a statistical average over the magnetic interactions of the occupied states). In these complexes it is therefore assumed that the symmetry of the complexes is lower than O_h, possibly D_{4h} or C_{3v} and the field strength of the ligands are such as to make the quartet or sextet spin state near the doublet spin ground state. The excited state being partially populated by the complex molecules, will thus, contribute to the magnetic moments making their values relatively high. In other cases where the values of the magnetic moment lie below 2.31 B.M., these states (quartet or sextet) may be relatively far from the ground state and their contribution to the magnetic moment will be relatively less. The lowering of the symmetry from O_h towards D_{4h} or C_{3v} in all the complexes is also indicated by the esr studies. Also, the esr studies of the complex [$RuCl_2(dbm)(PPh_3)_2$] suggested the quartet state to lie near the ground doublet spin state.

Electron Spin Resonance Spectra

All the complexes except three exhibit spectra characteristic of an axially symmetric complex with $g_{\parallel}$ around 1.81 - 1.94

and $g_\perp$ around 2.26-2.46 (Table IV.3). The average $<g>$ value turns out to be in the range of 2.14-2.28. In chloroform solution there is practically no change in the esr spectra of these complexes.

The spectra of the other set of three complexes, viz., $[RuCl_2(ba)(PPh_3)_2]$, $[RuCl_2(dbm)(PPh_3)_2]$ and $[RuBr_2(dbm)(AsPh_3)_2]$ were different from those of the previous set. The spectrum of $[RuCl_2(ba)(PPh_3)_2]$ exhibited three bands with $g_1 = 2.3470$, $g_2 = 1.9373$ and $g_3 = 1.8563$. The spectrum of $[RuCl_2(dbm)(PPh_3)_2]$ showed five bands while that of $[RuBr_2(dbm)(AsPh_3)_2]$ six bands (Fig. IV.3). In the spectrum of $[RuCl_2(dbm)(PPh_3)_2]$ there also appeared a band due to half-field transition.

The ground state of ruthenium(III) is $^2T_{2g}$ in the strong cubic field. It is split into two states by a tetragonal field, a doubly degenerate $^2B_2$ state and a four fold degenerate ^2E state. These have a total energy separation of δ which is defined as the tetragonal field strength. First order spin orbit coupling within these states further splits the ^2E states into two doubly degenerate spin states. As a result of these interactions and the interactions in the magnetic field, it can be shown that in an octahedral field with tetragonal distortion, $g_x = g_y \neq g_z$ and one should, thus, expect two values for 'g'.[16] A mathematical expression to calculate the values of $g_\perp$ and $g_\parallel$ for low spin d^5 system having octahedral symmetry with tetragonal distortion has been given.[17] It was shown that in cases

Table IV.3

Electron spin resonance spectral data

Sl. No.	Complex	$g_\perp$	$g_\parallel$	$\langle g \rangle$
1.	$RuCl_2(acac)(AsPh_3)_2$	2,3070	1.8848	2.1663
2.	$RuCl_2(dbm)(AsPh_3)_2$	2.2667	1.8688	2.1341
3.	$RuCl_2(ba)(AsPh_3)_2$	2.2998	1.8136	2.1344
4.	$RuCl_2(acac)(PPh_3)_2$	2,3470	1.9423	2.2121
5.	$RuBr_2(acac)(AsPh_3)_2$	2.3674	1.9247	2.2198
6.	$RuBr_2(ba)(AsPh_3)_2$	2.3674	1.9373	2.2240
7.	$RuBr_2(acac)(PPh_3)_2$	2.4601	1.9076	2.2759
8.	$RuBr_2(dbm)(PPh_3)_2$	2.4086	1.9263	2.2478
9.	$RuBr_2(ba)(PPh_3)_2$	2.3866	1.9122	2.2285

-1/2, +1/2. In such a case, transitions $\mp 1/2 \rightarrow \pm 3/2$ may be expected besides other normal transitions with $\Delta M_s = \pm 1$. The number of transitions with $\Delta M_s = \pm 1$ will, under these conditions, be more than three in number. In the spectrum of our complex, the presence of five bands conforms with the assumption made to explain the band due to half-field transition. The value of magnetic moment for this complex was found to be 2.71 B.M. which is much higher than the spin only value for one unpaired electron (1.73 B.M.). The higher value of the magnetic moment also indicates the presence of a low lying quartet state which is thermally populated by the complex molecules. Because of the partial occupation of this state by the molecules, the statistical average over the magnetic interaction of the occupied state will give higher value for the magnetic moment of the complex ($\mu = 2.71$ B.M.). In the other complexes the energy difference between this state (quartet spin) and doublet spin state may be relatively large and therefore, the contribution to the magnetic susceptibility due to this state will be relatively less. This will result in relatively lower values of the magnetic moments of other complexes as compared to 2.71 B.M. Also the absence of more than two bands and the band due to half-field transition in these complexes suggested the larger energy separation between the ground double and the next excited quartet spin states. Here we have not taken into account the sextet state. The presence of sextet state should give one of the 'g'

values around 5.[18,19] Since the experimental value of 'g'

does not exceed more than 2.65, it is therefore, assumed that

the sextet state is possibly not the next higher state.

In the spectrum of $[RuBr_2(dbm)(AsPh_3)_2]$ six bands with

'g' values ranging from 1.57 to 5.23 have been observed. The

higher value of 'g' viz., 5.23 could only be explained by assu-

ming the sextet spin state lying near the ground doublet spin

state.[18,19] However, this assumption could not explain the low

value of magnetic moment (2.1 B.M.). Even if one assumes the

ground state contribution to the magnetic moment of the complex

as 1.73 B.M. (spin only value) and the remaining contribution

(0.37 B.M.) due to the presence of sextet state next to the

doublet state, it is not very reasonable to explain the value

of magnetic moment. At this stage it is not possible to give

a reasonable explanation for the appearance of six bands in the

spectrum of the complex.

It is to be pointed out here that the above discussion of

the esr spectra of the complexes is only tentative.

Electronic Spectra

The electronic spectra of all the complexes in chloroform

solution showed two to three bands around 600, 500 and 400 nm

(Table IV.4 and Figs. IV.4 and IV.5). These bands are very

much characteristic of the octahedral surrounding of the ligand

Table IV.4

Electronic spectral data of the complexes

Sl. No.	Complex	λ_{max} nm	ε	Assignment
1	2	3	4	5
1.	$RuCl_2(acac)(AsPh_3)_2$	585	220	$^2T_{2g} \rightarrow {}^2A_{2g}$
		385	3,310	Charge Transfer
2.	$RuCl_2(dbm)(AsPh_3)_2$	595	225	$^2T_{2g} \rightarrow {}^2A_{2g}$
		395	3,400	Charge Transfer
3.	$RuCl_2(ba)(AsPh_3)_2$	592	195	$^2T_{2g} \rightarrow {}^2A_{2g}$
		390	4,935	Charge Transfer
4.	$RuCl_2(acac)(PPh_3)_2$	605	195	$^2T_{2g} \rightarrow {}^2A_{2g}$
		390	2,180	Charge Transfer
5.	$RuCl_2(dbm)(PPh_3)_2$	615	75	$^2T_{2g} \rightarrow {}^2A_{2g}$
		390	2,980	Charge Transfer
6.	$RuCl_2(ba)(PPh_3)_2$	600	300	$^2T_{2g} \rightarrow {}^2A_{2g}$
		390	3,070	Charge Transfer
		360	4,675	"
7.	$RuBr_2(acac)(AsPh_3)_2$	640	245	$^2T_{2g} \rightarrow {}^2A_{2g}$
		490	1,690	Charge Transfer
		405	2,320	"
8.	$RuBr_2(dbm)(AsPh_3)_2$	650	316	$^2T_{2g} \rightarrow {}^2A_{2g}$
		475	2,620	Charge Transfer
		400	2,550	"

Table IV.4 (contd.)

1	2	3	4	5
9.	$RuBr_2(ba)(AsPh_3)_2$	645	380	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		485	2,070	Charge Transfer
		380	4,350	"
10.	$RuBr_2(acac)(PPh_3)_2$	655	265	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		495	2,045	Charge Transfer
		410	3,190	"
11.	$RuBr_2(dbm)(PPh_3)_2$	655	260	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		470	1,885	Charge Transfer
		420	3,300	"
12.	$RuBr_2(ba)(PPh_3)_2$	655	255	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		475	1,520	Charge Transfer
		415	2,365	"

molecules around the ruthenium(III) ions.[15,20,21] Generally in the visible region ruthenium(III) ion shows charge transfer bands.[21] The bands around 600, 500 and 400 nm could be assigned to charge transfer bands. However, the value of the extinction coefficients of the band around 600 nm is low (≈ 250) indicating the possibility of its being due to ligand field transition. In the octahedral symmetry one spin allowed transition should appear due to $^2T_{2g} \rightarrow {}^2A_{2g}$ which should be split or unsymmetrical in a tetragonal or rhombic field. The shape of the band at 600 nm is also not symmetric. It is therefore preferred to assign the band around 600 nm due to ligand field transition and the bands around 500 nm and 400 nm to be due to charge transfer. The lowering of the symmetry from O_h towards D_{4h} or C_{3v} has also been indicated by the esr spectra.

The positions of all the bands in the bromo complexes shifted towards longer wavelength side. This may be due to the greater reducing power of Br^- than Cl^- whereby the positions of all the charge transfer bands shifted to longer wavelength (390 nm band $\rightarrow$ 500 nm). Further Br^- ion produces weaker field as compared to that of chloride ion and hence the ligand field transition shifted towards longer wavelength side (600 nm $\rightarrow$ 650 nm). Besides this shift, the following trends have been observed for the band around 600 nm ($^2T_{2g} \rightarrow {}^2A_{2g}$):

(i) The positions of the bands in phosphine complexes shifted towards longer wavelength as compared to those of arsine.

(ii) The positions of the bands in dibenzoylmethanate, benzoylacetonate and acetylacetonate complexes are shifted progressively towards shorter wavelength side.

Thus on the basis of the ir, electronic and esr spectral data, the following geometries are postulated for the complexes:

$RuCl_2(acac)(AsPh_3)_2$	D_{4h} (octahedral geometry with tetragonal distortion)
$RuCl_2(dbm)(AsPh_3)_2$	"
$RuCl_2(ba)(AsPh_3)_2$	"
$RuCl_2(acac)(PPh_3)_2$	"
$RuBr_2(acac)(AsPh_3)_2$	"
$RuBr_2(ba)(AsPh_3)_2$	"
$RuBr_2(acac)(PPh_3)_2$	"
$RuBr_2(dbm)(PPh_3)_2$	"
$RuBr_2(ba)(PPh_3)_2$	"
$RuCl_2(ba)(PPh_3)_2$	Octahedral geometry with rhombic distortion

$\left[RuCl_2(acac)(AsPh_3)_2 \right]$

$\left[RuCl_2(dbm)(AsPh_3)_2 \right]$

$\left[RuCl_2(ba)(AsPh_3)_2 \right]$

$\left[RuCl_2(acac)(PPh_3)_2 \right]$

DPPH
g = 2.0036

H $\longrightarrow$

Fig. IV.1 ESR SPECTRA

$[RuBr_2(acac)(PPh_3)_2]$

$[RuBr_2(dbm)(PPh_3)_2]$

$[RuBr_2(ba)(PPh_3)_2]$

H ⟶

DPPH
g = 2.0036

$[RuBr_2(ba)(AsPh_3)_2]$

Fig. IV.2 ESR SPECTRA

$\left[RuBr_2(dbm)(AsPh_3)_2\right]$

DPPH

$\left[RuCl_2(dbm)(PPh_3)_2\right]$

DPPH

H →

680 G
2 cm
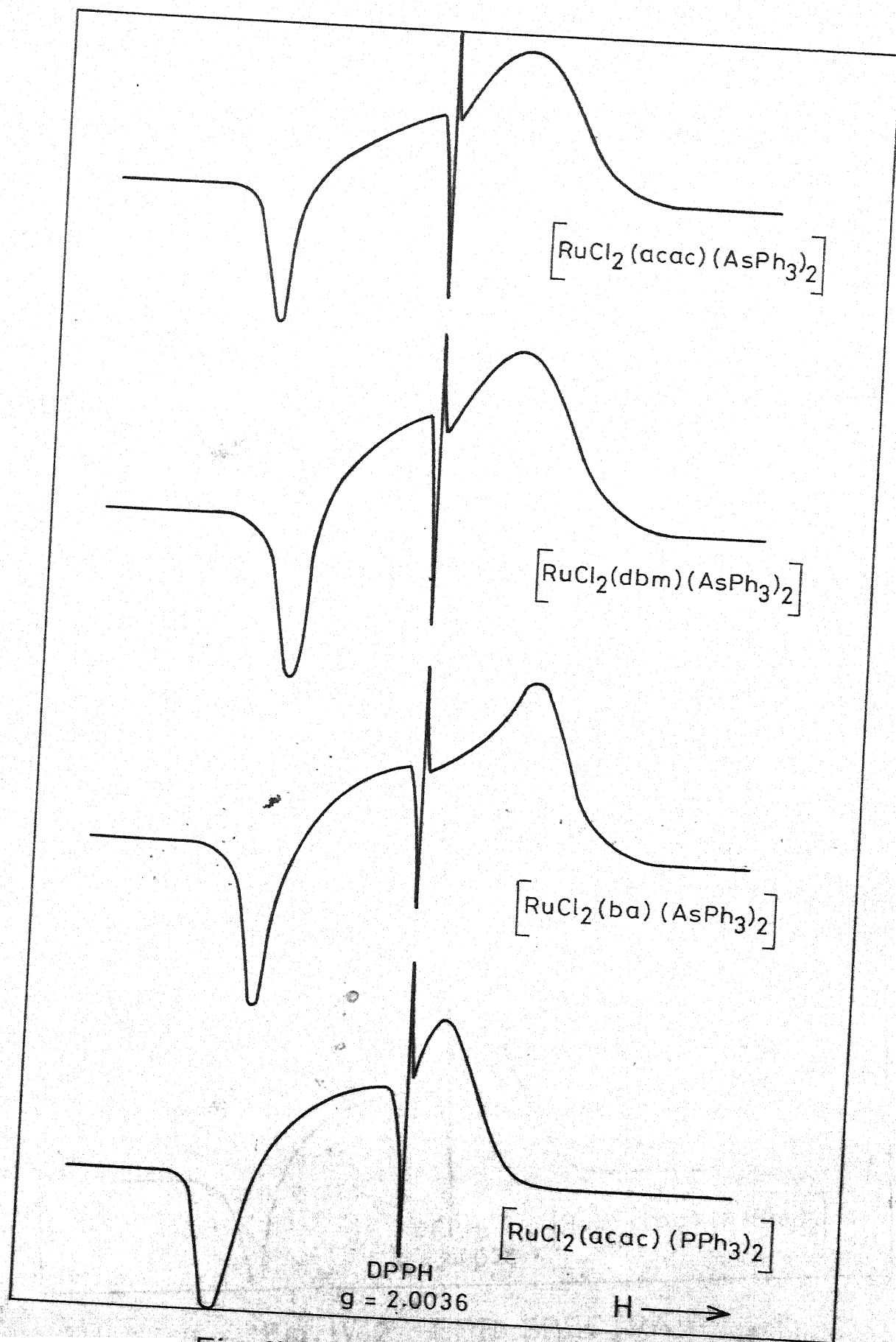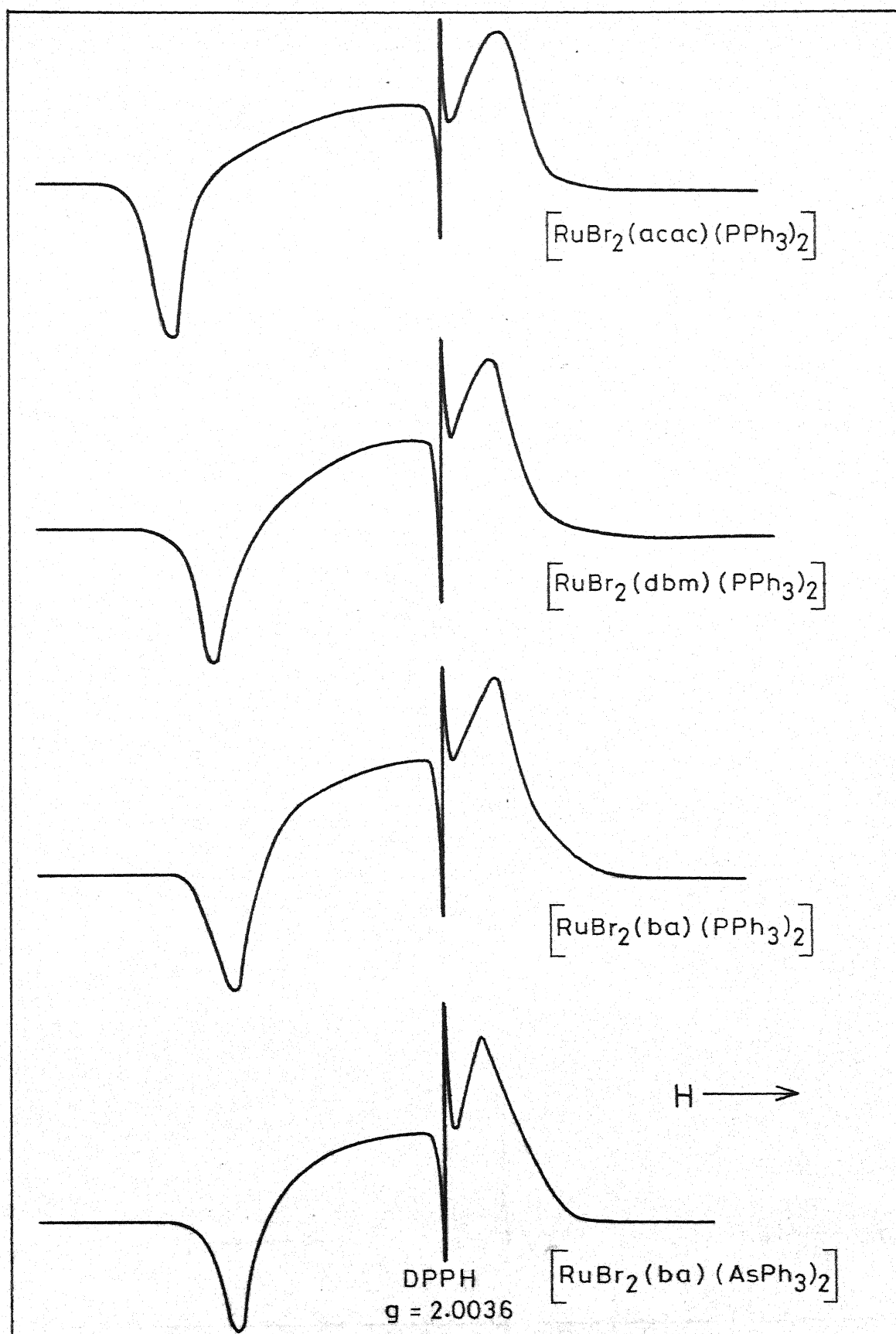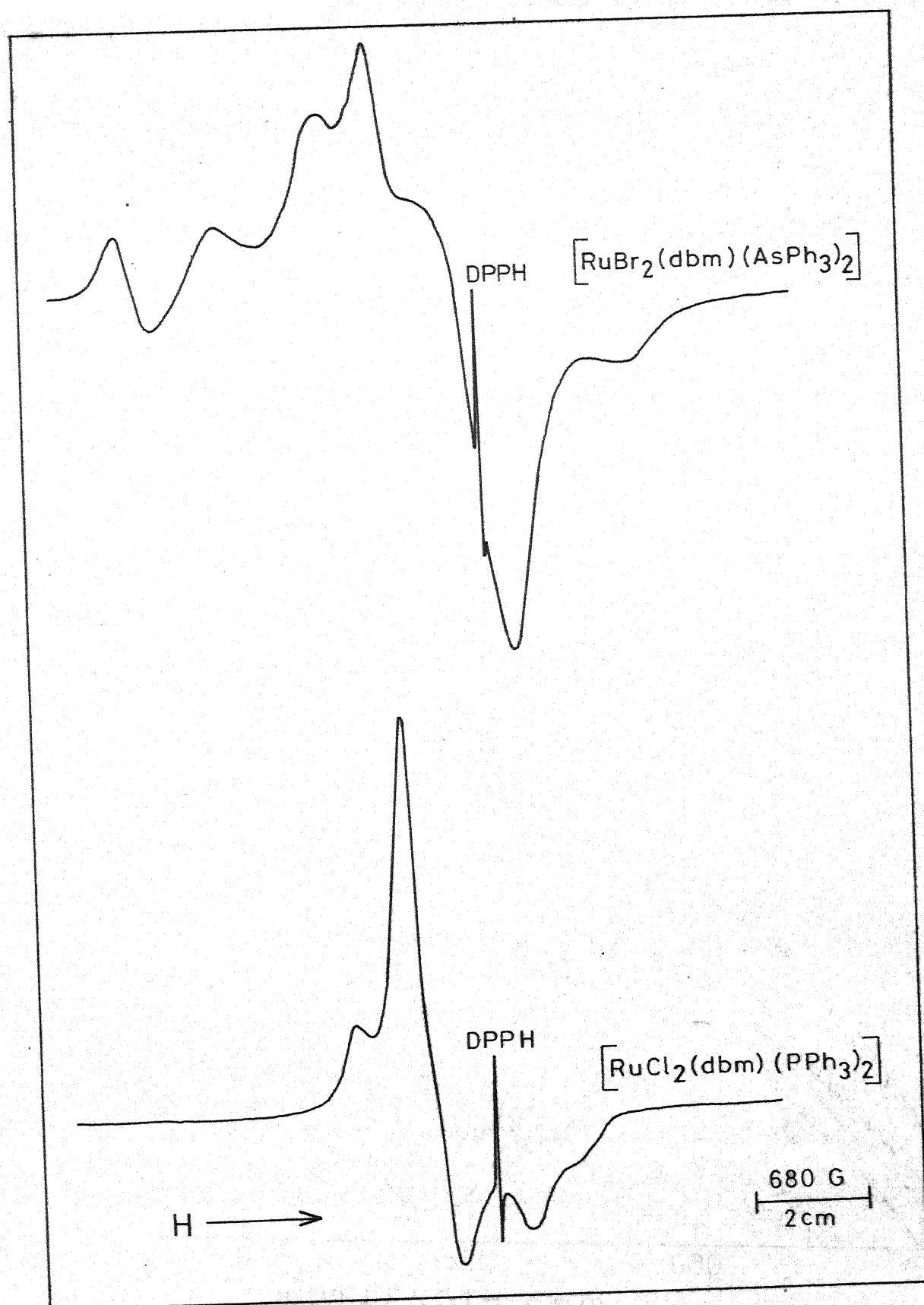
Fig. IV.3   ESR SPECTRA

Fig. IV.4 ELECTRONIC SPECTRA

① RuCl$_2$(acac)(AsPh$_3$)$_2$
② RuCl$_2$(dbm)(AsPh$_3$)$_2$
③ RuCl$_2$(acac)(PPh$_3$)$_2$
④ RuCl$_2$(ba)(PPh$_3$)$_2$
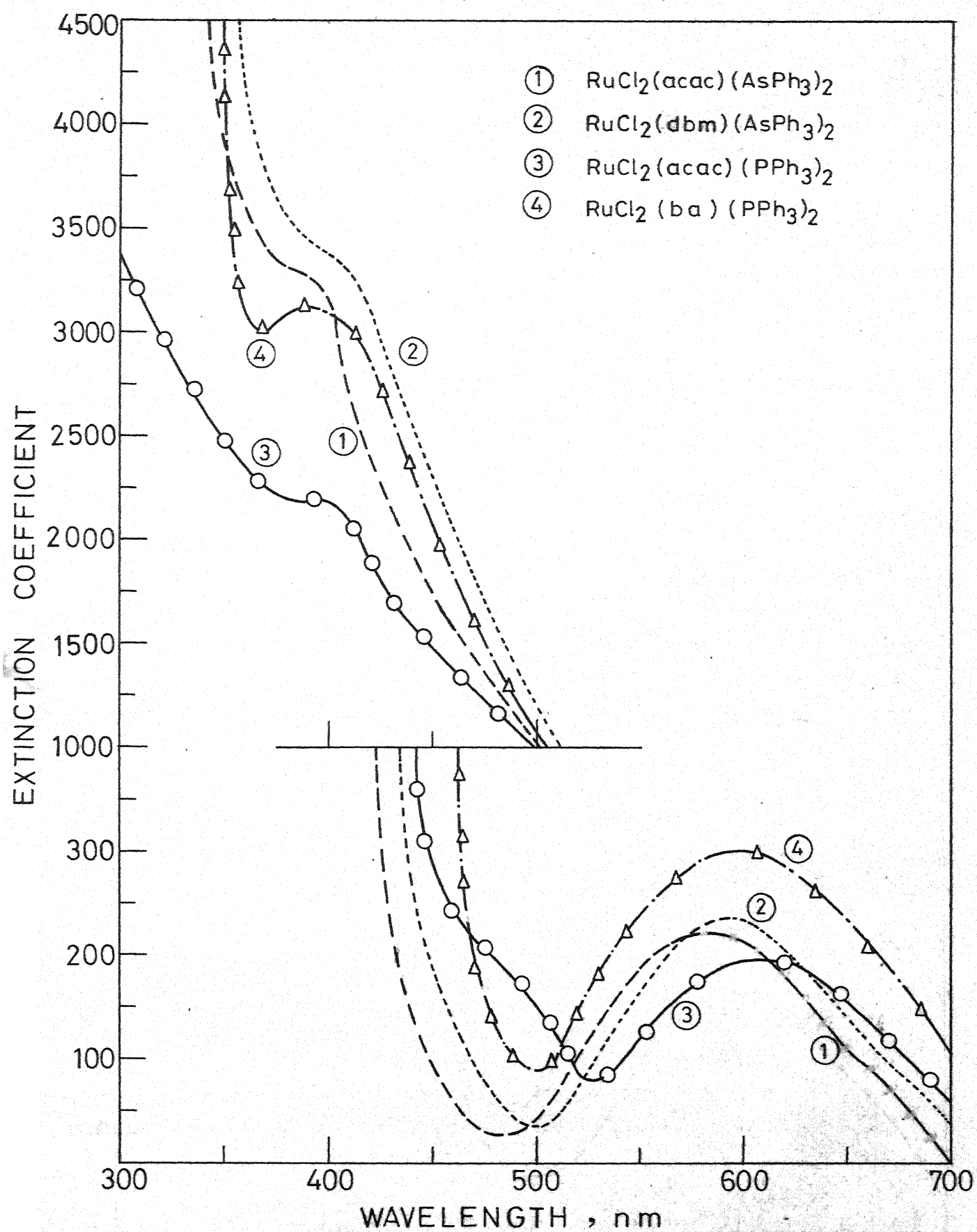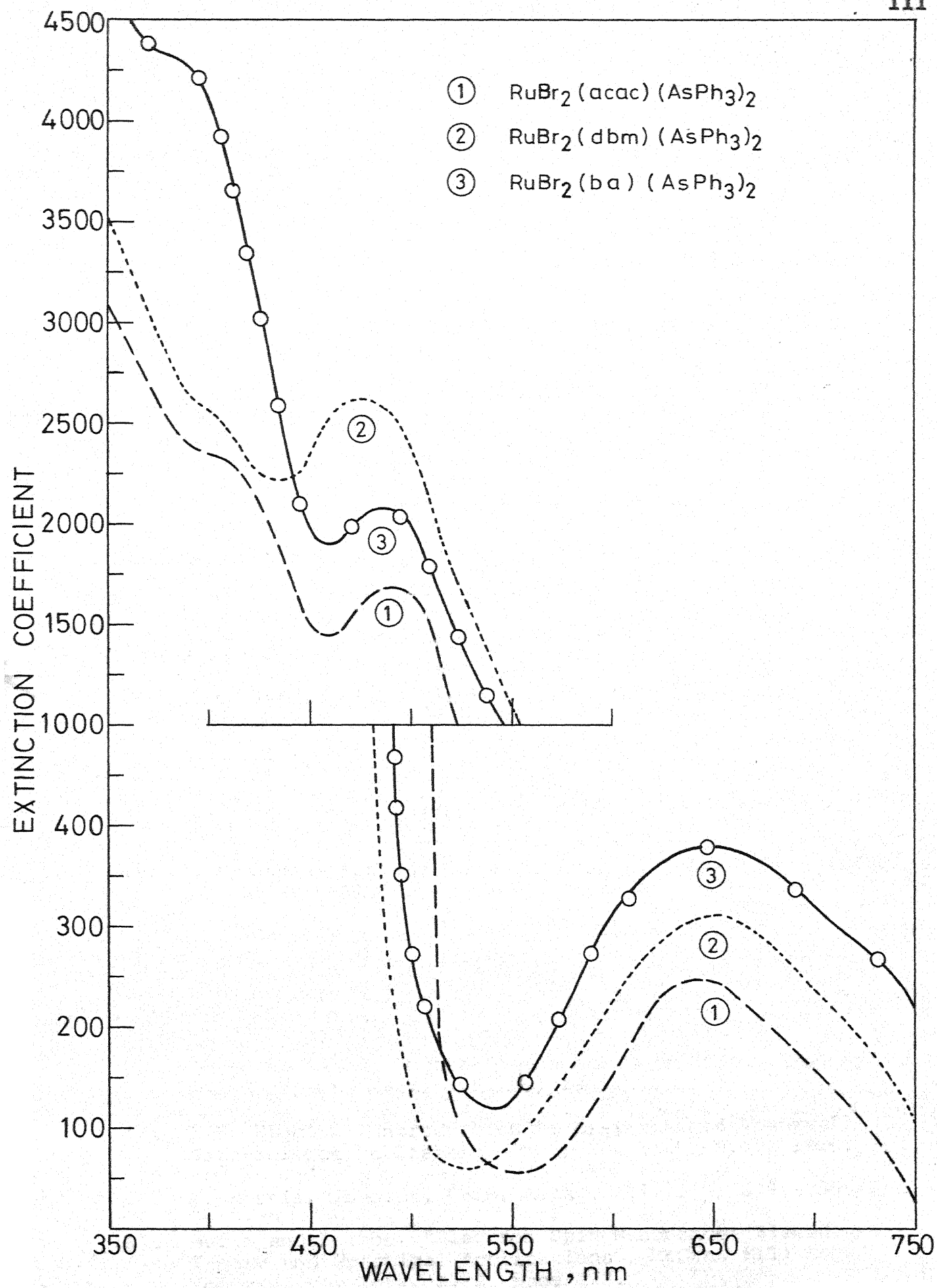
Fig .IV .5 ELECTRONIC SPECTRA

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CHAPTER   V

RUTHENIUM(III) AND RUTHENIUM(II)
COMPLEXES CONTAINING TRIPHENYLARSINE
AND TRIPHENYLARSINE OXIDE

A wide variety of ruthenium(II) complexes with tertiary-phosphines and arsines have been synthesized.[1] Only a few analogous ruthenium(III) complexes are known.[2] In this chapter further investigations on the ruthenium(III) complex $[RuCl_3(AsPh_3)(OAsPh_3)_2]$[3] have been reported. From these studies it has been concluded that the formula of the compound should have been $[RuCl_3(AsPh_3)_2(OAsPh_3)]$ rather than $[RuCl_3(AsPh_3)(OAsPh_3)_2]$ as has been erroneously reported earlier.[3] A new isomer of $[RuCl_3(AsPh_3)_3]$ besides other new compounds is also reported.

EXPERIMENTAL

All the reagents used were of chemically pure or Analar grade.

Trichloro-bis(triphenylarsine)(methanol)ruthenium(III) was prepared by the method described in the literature.[4]

PREPARATIONS OF COMPLEXES

(a) Ruthenium(III) Complexes

(i) Trichloro-tris(triphenylarsine)ruthenium(III), [RuCl$_3$(AsPh$_3$)$_3$]

0.3 g of triphenylarsine was added to a solution of [RuCl$_3$(AsPh$_3$)$_2$.MeOH] (0.2 g) in 10 ml of benzene. It was heated under reflux in nitrogen atmosphere for 1 hr and then filtered. The filtrate was kept for 6 hr at 0°C whereby pink crystals appeared. These were filtered out, washed with benzene and ether and dried.

(ii) Trichloro-bis(triphenylarsine)(triphenylarsine oxide)-
ruthenium(III), [RuCl$_3$(AsPh$_3$)$_2$(OAsPh$_3$)]:

0.2 g of triphenylarsine was added to a solution of [RuCl$_3$(AsPh$_3$)$_2$.MeOH] (0.2 g) in 30 ml of benzene. It was heated under reflux in the presence of oxygen for 2 hr whereupon a reddish brown compound was obtained. It was filtered, washed with benzene and ether and dried under vacuum.

(iii) Trichloro-bis(triphenylarsine)ruthenium(III),[RuCl$_3$(AsPh$_3$)$_2$]:

0.2 g of[RuCl$_3$(AsPh$_3$)$_2$.MeOH]was taken in 10 ml of benzene to which 0.1 g of triphenylarsine was added. It was heated under reflux in nitrogen atmosphere for 1 hr. A dark brown compound separated. It was filtered and washed with ether and dried under vacuum.

(b) Ruthenium(II) Complexes

(i) Trichloro nitrosyl(triphenylarsine)(triphenylarsine oxide)-ruthenium(II), [RuCl$_3$(NO)(AsPh$_3$)(OAsPh$_3$)]:

0.3 g of [RuCl$_3$(AsPh$_3$)$_2$(OAsPh$_3$)]was dissolved in 10 ml of dichloromethane and nitric oxide gas was passed into the solution for about two hours whereby the colour of the solution changed to light pink. The solution was then concentrated to about one ml and ether was added to it. A light pink compound precipitated out. It was filtered and washed with ether and dried under vacuum.

(ii) Dichloro-dicarbonyl(triphenylarsine)(triphenylarsine oxide)-ruthenium(II), [RuCl$_2$(CO)$_2$(AsPh$_3$)(OAsPh$_3$)]:

0.2 g of [RuCl$_3$(AsPh$_3$)$_2$(OAsPh$_3$)] was dissolved in 10 ml of dichloromethane and carbon monoxide gas was passed into the solution for about 2 hr. The solution became light yellow in colour. After concentrating the solution to about one ml, petroleum ether

was added whereby a yellow compound precipitated. It was fil-
tered and washed with petroleum ether and dried under vacuum.
It was recrystallized from dichloromethane - petroleum ether
mixture.

The percentage of halide present in the complexes was
determined by the standard method.[5] Carbon, hydrogen and nitro-
gen analyses, melting points, electronic spectra and magnetic
measurements were obtained according to the methods described
in Chapter II. Infrared spectra were recorded using Perkin-
Elmer 521 in the range of 4000-300 cm^{-1} and Perkin-Elmer Infra-
cord in the range of 4000-700 cm^{-1}. The electron spin reso-
nance spectra of the compounds were taken using Varian Associates
Model V-4502 esr Spectrophotometer at room temperature. The
results are given in Tables V.1 and V.2.

RESULTS AND DISCUSSION

(1) Complex [$RuCl_3(AsPh_3)_2(OAsPh_3)$]

This complex was earlier[3] formulated as [$RuCl_3(AsPh_3)$-
$(OAsPh_3)_2$] on the basis of ir and chemical reactions with pyri-
dine. The reinvestigations, however, revealed that the
complex should be formulated as [$RuCl_3(AsPh_3)_2(OAsPh_3)$]. This
was further confirmed by the following experimental results:

(i) The ir spectrum of the compound [$RuCl_3(AsPh_3)_2(OAsPh_3)$]
showed a band at 880 cm^{-1} indicating the presence of triphenyl-

Table V.1

Analytical data, metling point, colour and magnetic moment of the complexes

Complex	Colour	M.P. °C	Analyses calculated (%)				Analyses found (%)				$\mu_{eff.}$ B.M.
			C	H	N	Cl	C	H	N	Cl	
$RuCl_3(AsPh_3)_2(OAsPh_3)$	Reddish-brown	218	56.77	3.94	–	9.32	56.12	3.82	–	9.64	2.80
$RuCl_3(AsPh_3)_3$	Pink	166–68	57.53	3.99	–	9.45	57.72	4.11	–	9.88	2.10
$RuCl_3(AsPh_3)_3$ [a]	Brown	172	57.53	3.99	–	9.45	57.40	4.00	–	9.90	1.90
$RuCl_3(AsPh_3)_2$	Dark-brown	>290	52.72	3.66	–	12.98	53.21	3.69	–	13.41	2.20
$RuCl_3(NO)(AsPh_3)(OAsPh_3)$	Pink	104	49.92	3.47	1.62	12.30	50.02	3.31	1.57	12.38	D
$RuCl_2(CO)_2(AsPh_3)(OAsPh_3)$	Yellow	84	50.47	3.50	–	8.28	50.07	3.61	–	8.52	D

D = diamagnetic;   a, Ref. no. 3.

arsine oxide ($v_{As=O}$ around 880 cm^{-1}) in the complex.

(ii) The reactions of the complex with a number of coordinating solvents e.g., CH_3CN, $CH_3CH_2CH_2CN$, dmf and dmso yielded compounds having the general formula [$RuCl_3(AsPh_3)_2L$][6,7] (L = solvent molecule). The ir spectra of these compounds did not show any band around 880 cm^{-1}. These compounds and the ones described in Chapter II having the same empirical formulae were identical.

(iii) Its reactions with tetraphenylarsonium chloride and tetramethylammonium chloride gave $Ph_4As[RuCl_4(AsPh_3)_2].2Me_2CO$ and $Me_4N[RuCl_4(AsPh_3)_2]$ respectively.[8]

(iv) One of the reaction products isolated after the completion of the reactions described in (ii) and (iii) was found to be triphenylarsine oxide.

Since in the above reactions (cf. (ii)) one molecule of the solvent replaced one molecule of triphenylarsine oxide from the complex to form [$RuCl_3(AsPh_3)_2L$], leaving triphenylarsine oxide in the reaction medium, only one molecule of triphenylarsine oxide rather than two should be present in the complex. The formula of the original compound should therefore be $[RuCl_3(AsPh_3)_2(OAsPh_3)]$.

The experimental value of magnetic moment of [$RuCl_3(AsPh_3)_2$ (OAsPh_3)] is 2.80 B.M. It is very much higher than predicted theoretically for Ru^{3+} with one unpaired electron. In order to

explain this it is assumed that in this compound the ligand field strength around Ru^{3+} and symmetry are close to spin transition region and small changes in the conditions are enough to make the ground state of Ru^{3+} somewhere in between $^2T_{2g}$ and $^4T_{2g}$ or $^6A_{1g}$. This will tend to increase the value of the magnetic moment high. A few examples of Ru^{3+} complexes having higher values of magnetic moment have been reported in the literature.[9] It is equally possible that the ruthenium may exist in +4 state as an impurity in the complex which will increase the value of magnetic moment of the complex. This has been ruled out by the fact that the magnetic moment values of the complexes $[RuCl_3(AsPh_3)_2L]$ $(L = CH_3CN$ etc.) and the complexes formed by the reactions of this complex with various ligands were found to be normal ($\simeq 2.0$ B.M.).

The esr spectrum of the compound $[RuCl_3(AsPh_3)_2(OAsPh_3)]$ in the powdered form taken at room temperature showed three absorption lines (Fig. V.1). The g values have been calculated taking DPPH 'g' value as 2.0036. The calculated values of 'g' from the spectrum were, $g_x = 2.4266$, $g_y = 2.1754$ and $g_z = 1.6731$. These values correspond with those found for other ruthenium(III) complexes having C_{2v} symmetry.[10] For the complexes $[MA_3B_3]$ having C_{2v} symmetry, $g_{zz} \neq g_{xx} \neq g_{yy}$ and so there will be three absorption lines in the esr spectra. On the basis of the number of lines and the values of 'g', following distorted octahedral structure has been assigned to this complex.

Cl

Ph₃As   Cl

                Ru

Cl   AsPh₃
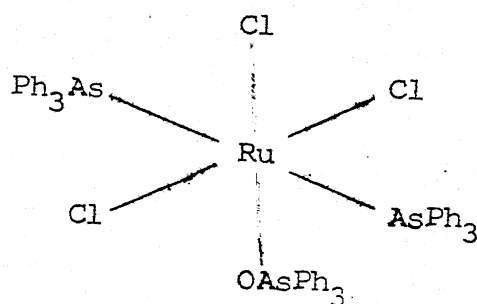
            OAsPh₃

(2) Carbonyl and Nitrosyl Complexes

The reactions of [RuCl₃(AsPh₃)₂(OAsPh₃)] with nitric oxide

and carbon monoxide are very interesting. The analytical data

indicated the formation of two new complexes [RuCl₃(NO)(AsPh₃)-

(OAsPh₃)] and [RuCl₂(CO)₂(AsPh₃)(OAsPh₃)] as a result of the

reactions. Both the complexes were found to be diamagnetic

indicating ruthenium to be present in +2 oxidation state in the

complexes. The diamagnetic behaviour of the complex

[RuCl₃(NO)(AsPh₃)(OAsPh₃)] could only be explained if one assumes

that nitric oxide molecule is bonded to ruthenium as NO⁺. This

is further substantiated by the ir data.

The positions of the major ir bands in the spectra of

these complexes and the probable assignments are as follows:

(a) All the characteristic bands due to triphenylarsine

were present in the spectra.

(b) In the spectra of both the complexes the bands due to

$\nu_{As=O}$ were present at 870 cm⁻¹ indicating the presence of tri-

phenylarsine oxide.

(c) The spectrum of the carbonyl complex $[RuCl_2(CO)_2-(AsPh_3)(OAsPh_3)]$ showed two strong and sharp bands at 1980 cm^{-1} & 2090 cm^{-1}. These were assigned to $\nu_{sy}(CO)$ and $\nu_{asy}(CO)$ respectively. The positions of these bands indicated that the two carbonyl groups are terminal and linked in the cis-position.[11]

(d) The spectrum of the nitrosyl complex showed one strong and sharp band at 1860 cm^{-1}. This has been assigned to $\nu_{(NO)}$.[12] The position of this band indicates that NO is linked with the metal ion as NO^+.[12]

The following interesting points are worth noting in these complexes:

(i) Unlike other complexes formed by the reactions of $[RuCl_3(AsPh_3)_2(OAsPh_3)]$ with coordinating solvents (Section 1(ii)) triphenylarsine oxide remains bonded with ruthenium in the carbonyl and nitrosyl complexes.

(ii) Ruthenium is reduced from +3 to +2 oxidation state.

(iii) When $[RuCl_3(NO)(AsPh_3)(OAsPh_3)]$ was dissolved in benzene and refluxed with triphenylarsine, the well characterised complex $[RuCl_3(NO)(AsPh_3)_2]$[12] was obtained and in the filtrate the triphenylarsine oxide was separated and identified.

(3) $[RuCl_3(AsPh_3)_3]$ (pink)

The analytical data indicate that the empirical formula of the complex is $[RuCl_3(AsPh_3)_3]$ which is similar to that of

the brown compound described in the literature.[3] This compound could therefore be either a polymer or oligomer or an isomer of the brown compound. Since the preferential geometry found in Ru^{3+} complexes is octahedral having six coordination sites, it is quite unlikely that the complex $[RuCl_3(AsPh_3)_3]$, having six discrete donors, will be polymeric or oligomeric. It is, therefore, assumed that it is different isomer of the well characterised brown complex $[RuCl_3(AsPh_3)_3]$. To substantiate this assumption and to derive a plausible structure of the complex, the following experiments were performed.

The pink compound $[RuCl_3(AsPh_3)_3]$ was allowed to react with various coordinating solvents like CH_3CN, $CH_3CH_2CH_2CN$, dmf and dmso. The compounds formed as a result of these reactions have the general formula $[RuCl_3(AsPh_3)_2L]$ (L = solvent molecule) identical to those which were obtained by reacting $[RuCl_3(AsPh_3)_3]$ (brown) with the respective solvents.[7] This suggested that the brown and the pink compounds are similar in nature. The two compounds were not identical was further corroborated by the values of their magnetic moment (pink complex, 2.1 B.M.; brown complex, 1.9 B.M.) data. These values further indicate the oxidation state of ruthenium to be +3 in these complexes.

The esr spectra of these complexes (Fig. VI.1) have been taken at room temperature to decide their possible geometries. Since for a complex $[MA_3B_3]$ having C_{3v} symmetry, $g_{zz} \neq g_{xx} = g_{yy}$

and for a complex having C_{2v} symmetry $g_{zz} \neq g_{xx} \neq g_{yy}$, one should expect two values for 'g' in the first case and three values in the second case. The esr spectrum of the brown compound showed two absorption lines at $g_\perp = 2.4907$ and $g_{||} = 1.6913$. The value of $\langle g \rangle$ has been calculated to be 2.2242. The spectrum of the pink compound showed three lines and from the positions of these, the values of g_x, g_y and g_z were calculated to be 2.5382, 2.2627 and 1.7117 respectively. Based on the above esr study, the brown compound should have C_{3v} symmetry and the pink, C_{2v} symmetry. The following structures have therefore been postulated for the complexes:
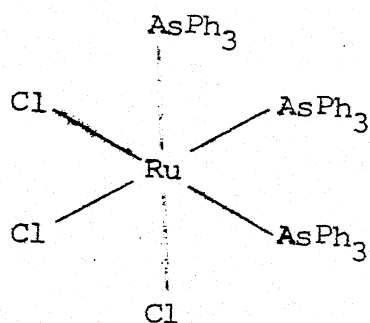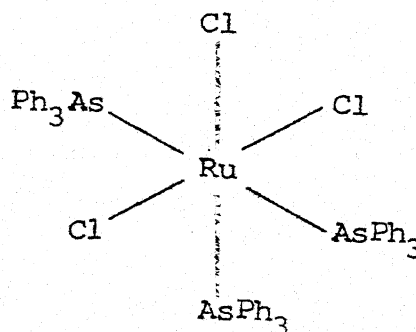
cis-C_{3v}	trans-C_{2v}
(Brown compound)	(Pink compound)

In order to explain the identical reaction products formed as a result of the reactions of both the complexes (pink and brown) with various coordinating solvents (e.g., CH_3CN, $CH_3CH_2CH_2CN$), the following dissociative mechanism out of many plausible ones has been tentatively assigned. First, one of the triphenylarsine

molecules/dissociates with the formation of a pentacoordinated species which in turn rearranges to the same pentacoordinate species in both the cases and finally a coordinating solvent molecule attaches itself to give the same hexacoordinated complex $[RuCl_3(AsPh_3)_2L]$.

(4) Complex $[RuCl_3(AsPh_3)_2]$

Reaction of $[RuCl_3(AsPh_3)_2.MeOH]$ with triphenylarsine under refluxing condition in benzene gave $[RuCl_3(AsPh_3)_2]$. The magnetic moment of this complex is 2.20 B.M. which indicates that ruthenium is present in +3 oxidation state with one unpaired electron. The same compound has also been reported by others.[6,13] The electronic spectra of this complex has been discussed in Chapter II.

ELECTRONIC SPECTRA

In the visible spectra of the octahedral complexes of spin paired d^5 system, low energy charge transfer bands ascribed to electron transfer from filled molecular orbitals mainly on the ligand to the hole available in the t_{2g} orbitals are prominent.[14-16] The spectra of all the complexes of ruthenium(III) showed a weak band around 500 nm and a number of moderately intense bands in the range of 300 to 400 nm. One should expect

Table V.2

Electronic spectral data of the complexes

Sl. No.	Complex	Chloroform solution			Nujol mull		Assignment
		λ nm	cm⁻¹	ϵ	λ nm	cm⁻¹	
1	2	3	4	5	6	7	8
1.	RuCl$_3$(AsPh$_3$)$_2$(OAsPh$_3$)	810	12345	322	–	–	–
		475	21053	820	520	19230	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		410	24390	1517	451	22222	Charge Transfer
		350	28571	2033	380	26316	=
					330	30303	=
					300	33333	=
2.	RuCl$_3$(AsPh$_3$)$_3$ (Pink)	840	11905	272	–	–	–
		495	20202	712	540	18518	$^2T_{2g} \longrightarrow {}^2A_{2g}$
		425	23532	1495	440	22717	Charge Transfer
					410	24390	=
					390	25641	=
					340	29412	=

Table V.2

1	2	3	4	5	6	7	8	
3.	$RuCl_3(NO)(AsPh_3)(OAsPh_3)$	590	16950	17	-	-	$^1A_{1g} \longrightarrow ^3T_{1g}$	
		440	22717	63	450	22222	$^1A_{1g} \longrightarrow ^3T_{2g}$	
		410	24390	452	410	24390	$^1A_{1g} \longrightarrow ^1T_{1g}$	
4.	$RuCl_2(CO)_2(AsPh_3)(OAsPh_3)$	590	16950	18	-	-	$^1A_{1g} \longrightarrow ^3T_{1g}$	
		510	19607	74	450	22222	$^1A_{1g} \longrightarrow ^3T_{2g}$	
		415	24096	333	380	26316	$^1A_{1g} \longrightarrow ^1T_{1g}$	

two Laporte allowed bands ascribed to $L_\pi \rightarrow t_{2g}$ transition in the region 300-400 nm. However, the presence of four to five bands having similar extinction coefficient may be due to their splitting because of the large value of spin-orbit coupling constants.[14] The band around 500 nm may be either due to ligand field transition[17] or due to charge transfer corresponding to transition from one of the components of $\pi t_{1g} \rightarrow 4dt_{2g}$. It is very difficult to adjudicate this matter. The electronic spectra appeared to be similar to that for other octahedral complexes of ruthenium(III).[7] The band around 840 nm in solution spectra may be due to the pentacoordinate species present in solution which was absent in the Nujol mull spectra.[7]

The visible spectra of the d^6 complexes are not so complicated because the charge transfer bands appear in the high energy region.[18] The low energy bands could be safely assigned to ligand field bands $(t_{2g} \rightarrow e_g^1 t_{2g}^5)$. In this case one should expect four bands (two weak and two intense) corresponding to transition from $^1A_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. The visible spectra of the carbonyl and nitrosyl complexes showed two weak bands around 590 and 500 nm and strong band around 400 nm. The values of 10Dq, B, C and β are calculated from the positions of these bands.[19] The values of these constants are 27,668 cm^{-1}, 332 cm^{-1}, 3573 cm^{-1} and 0.51 respectively which are well within the range of the octahedral complexes of ruthenium(II).

$[RuCl_3 (AsPh_3)_3]$ Pink

$[RuCl_3(AsPh_3)_3]$ Brown

$[RuCl_3 (AsPh_3)_2 (OAsPh_3)]$
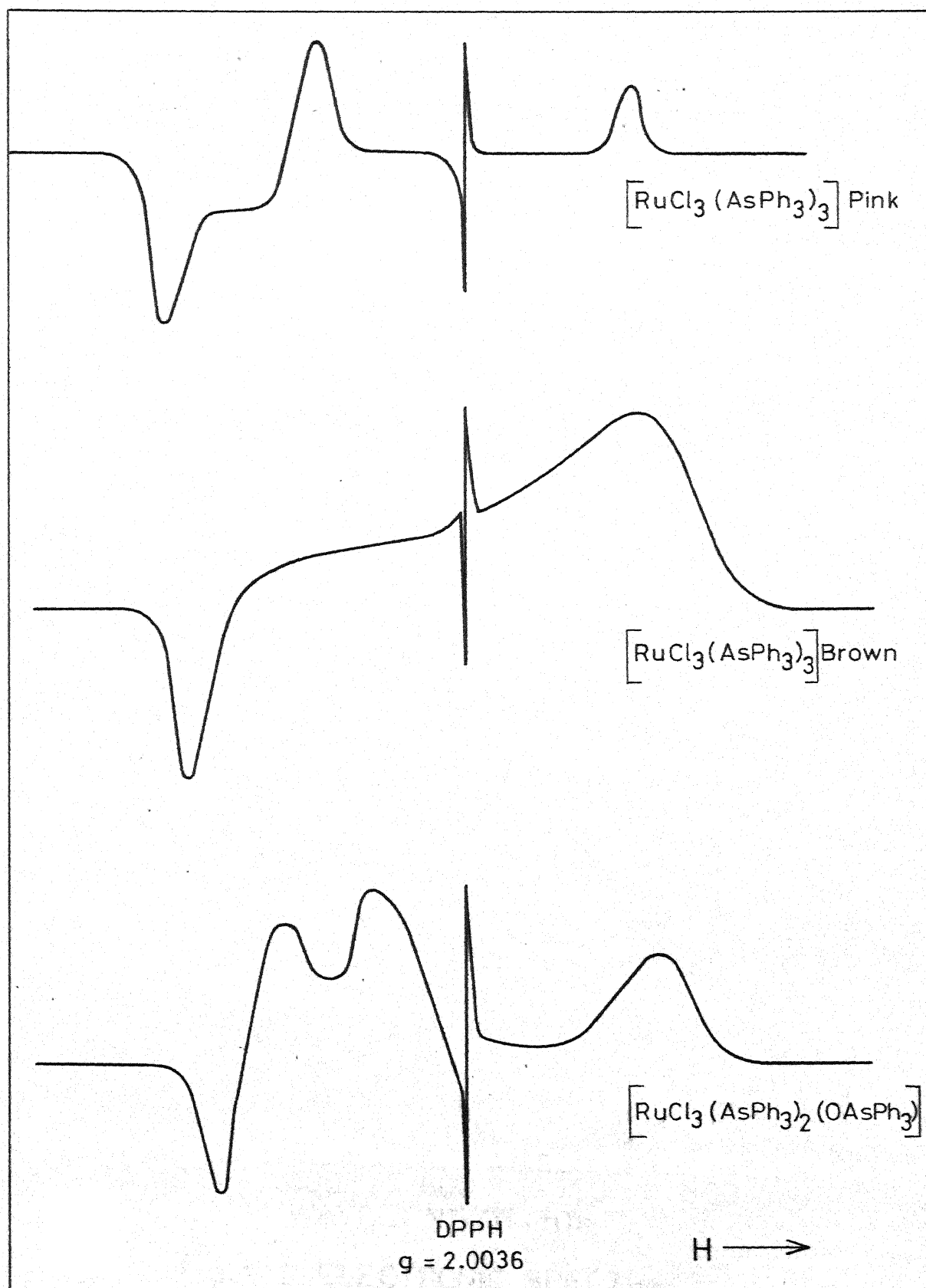
DPPH
g = 2.0036

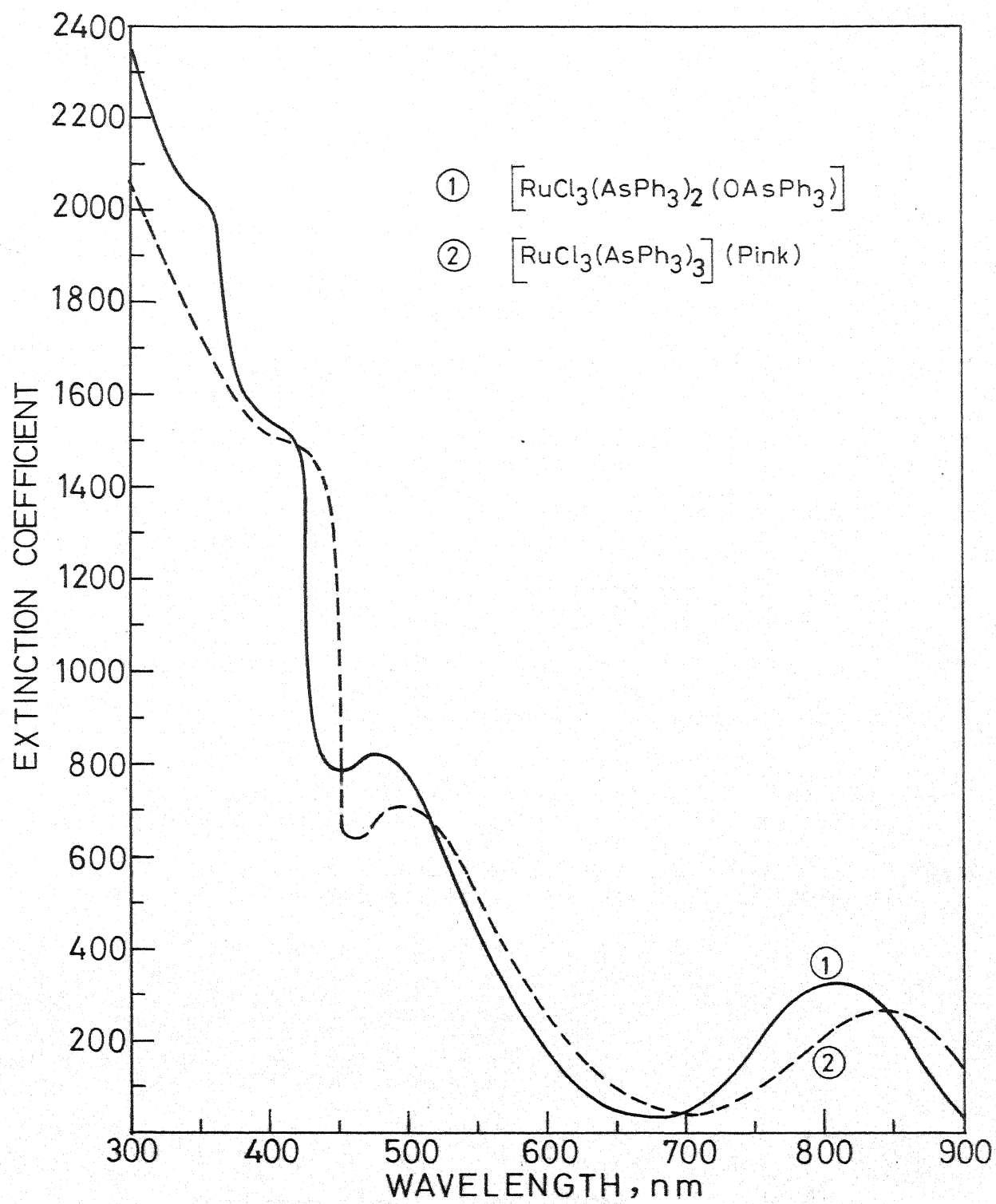H $\longrightarrow$

Fig. V.1   ESR   SPECTRA

Fig. V.2 ELECTRONIC SPECTRA

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CHAPTER VI

COMPLEXES OF RUTHENIUM(II) CONTAINING TRIPHENYLPHOSPHINE AND β-DIKETONES

A large number of complexes of ruthenium(II) containing triphenylphosphine and carboxylic acids as ligands are known in the literature,[1] but only a few analogous complexes of ruthenium(II) containing triphenylphosphine and β-diketones as ligands have been reported.[2] Chapter III and IV of this thesis describe reactions of β-diketones with triphenylphosphine and arsine complexes of ruthenium(II) and ruthenium(III). In this chapter the results of the interaction of β-diketones with $[RuH_2(CO)(PPh_3)_3]$ and $[RuHCl(CO)(PPh_3)_3]$ are reported.

EXPERIMENTAL

All the chemicals used were of chemically pure or Analar grade.

Carbonyldihydro-tris(triphenylphosphine)ruthenium(II) and
carbonylchlorohydrido-tris(triphenylphosphine)ruthenium(II) were
prepared according to the literature methods.[3]

PREPARATIONS

(i) Acetylacetonato hydrido carbonyl-bis(triphenylphosphine)-
ruthenium(II), $[RuH(acac)(CO)(PPh_3)_2]$:

A solution of acetylacetone (0.5 ml) in alcohol (5 ml) was
added to a solution of $[RuH_2(CO)(PPh_3)_3]$ (0.2 g) in benzene
(10 ml). The solution was heated under reflux for 3 hr whereby
a yellow solution was obtained. After concentrating the solu-
tion, petroleum ether was added and kept for slow crystalliza-
tion. Yellow crystals appeared. They were filtered, washed
with petroleum ether and dried under vacuum.

(ii) Dibenzoylmethanato hydrido carbonyl-bis(triphenylphosphine)-
ruthenium(II), $[RuH(dbm)(CO)(PPh_3)_2]$:

This complex was prepared by using a procedure similar
to (i) taking $[RuH_2(CO)(PPh_3)_3]$ and dibenzoylmethane.

(iii) Benzoylacetonato hydrido carbonyl-bis(triphenylphosphine)-
ruthenium(II), $[RuH(ba)(CO)(PPh_3)_2]$:

This complex was prepared by a similar procedure as des-
cribed in (i) taking $[RuH_2(CO)(PPh_3)_3]$ and benzoylacetone.

(iv) Acetylacetonato chloro carbonyl bis(triphenylphosphine)-ruthenium(II), [RuCl(acac)(CO)(PPh$_3$)$_2$] :

A solution of acetylacetone (0.5 ml) in ethanol (5 ml) was added to a solution of [RuHCl(CO)(PPh$_3$)$_3$](0.2 g) in benzene (10 ml). The mixture was heated under reflux for 3 hr whereby a yellow solution was obtained. On concentrating the solution, petroleum ether was added whereupon a yellow compound separated. It was filtered, washed with petroleum ether and dried under vacuum.

(v) Chloro-dibenzoylmethanato carbonyl-bis(triphenylphosphine)-ruthenium(II), [RuCl(dbm)(CO)(PPh$_3$)$_2$]:

This complex was prepared by a similar procedure as described in (iv) by taking [RuHCl(CO)(PPh$_3$)$_3$] and dibenzoylmethane.

(vi) Benzoylacetonato chloro carbonyl-bis(triphenylphosphine)-ruthenium(II), [RuCl(ba)(CO)(PPh$_3$)$_2$]:

This complex was prepared by the same procedure as in (iv) taking [RuHCl(CO)(PPh$_3$)$_3$] and benzoylacetone.

Carbon and hydrogen analyses, melting points, magnetic measurements, infared and electronic spectra were done as described in Chapter II. The chloride content in the complexes was determined by the standard method.[4]

The analytical results are given in Table VI.1.

RESULTS AND DISCUSSION

The analytical data indicate that as a result of the reactions of $[RuH_2(CO)(PPh_3)_3]$ with various β-diketones, one hydride ion and a molecule of triphenylphosphine were replaced from the original complex by a molecule of β-diketone to give complexes of the type $[RuH(bdk)(CO)(PPh_3)_2]$ (bdk = β-diketonate). Similarly by reacting $[RuHCl(CO)(PPh_3)_3]$ with β-diketones, one hydride ion and one molecule of triphenylphosphine were substituted by one molecule of β-diketone with the formations of $[RuCl(bdk)(CO)(PPh_3)_2]$.

Magnetic Susceptibility

All the complexes were diamagnetic indicating ruthenium in +2 oxidation state (d^6 system).

Infrared Spectra

The infrared spectra of the complexes $[RuH(bdk)(CO)(PPh_3)_2]$ showed bands around 2000, 1940, 1600, 1580 and 1530 cm^{-1} (Table VI.2) besides other characteristic bands due to triphenylphosphine and β-diketone. The band around 2000 cm^{-1} is assigned to $\nu_{(Ru-H)}$ and the one around 1940 cm^{-1} to $\nu_{(CO)}$ of the non-bridging carbonyl group.[5] The bands around 1600, 1580 and

Table VI.1

Analytical data, melting point and colour of the complexes

Sl. No.	Complex	Colour	M.P. °C	Analysis					
				Calculated (%)			Found (%)		
				C	H	Cl	C	H	Cl
1.	RuH(acac)(CO)(PPh$_2$)$_2$	Yellow	182	65.34	5.04	–	65.71	5.32	–
2.	RuH(dbm)(CO)(PPh$_3$)$_2$	"	208	71.15	4.78	–	70.74	5.32	–
3.	RuH(ba)(CO)(PPh$_3$)$_2$	"	154	67.72	4.90	–	68.01	4.75	–
4.	RuCl(acac)(CO)(PPh$_3$)$_2$	"	129	63.98	4.69	4.50	64.43	4.48	4.82
5.	RuCl(dbm)(CO)(PPh$_3$)$_2$	"	126	68.47	4.49	3.89	68.97	4.28	4.21
6.	RuCl(ba)(CO)(PPh$_3$)$_2$	"	120	64.97	4.59	4.17	64.39	4.15	4.41

acac = acetylacetonate;   dbm = dibenzoylmethanate;   ba = benzoylacetonate.

1530 cm^{-1} are the characteristic bands due to coordinated β-diketones which arise due to the normal coordinates having contributions from $\nu_{C=O}$ and $\nu_{C=C}$.[6]

The infrared spectra of the complexes $[\text{RuCl(bdk)(CO)(PPh}_3)_2]$ showed bands around 1980, 1600, 1575 and 1530 cm^{-1}. The strong and sharp band around 1980 cm^{-1} can be assigned to the ν_{CO} of the coordinated carbonyl group and the ones around 1600, 1575 and 1530 cm^{-1}, to the coordinated β-diketone.[6]

ELECTRONIC SPECTRA

All these complexes are found to be diamagnetic meaning thereby that their geometry ought to be pseudo octahedral. If one assumes the field around Ru^{2+} to be O_h symmetry, the ground state of ruthenium(II) (t_{2g}^6 configuration) should be $^1A_{1g}$. The excited state corresponding to $t_{2g}^5 e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ in increasing order of energy. Thus, four bands corresponding to the transitions from $^1A_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ should appear in the electronic spectra of the complexes. Regarding charge transfer bands, no band due to $L \rightarrow M$ transitions are possible in the visible region in the low spin d^6 system.[7] Also, because of the presence of carbonyl, hydride and phosphine as ligands capable of producing strong ligand field e_g^* levels, are relatively high in energy. As a result the bands due to charge transfer transitions $L_\pi \rightarrow e_g^*$

or $L\,\sigma_u \rightarrow e_g^*$ should lie in the high energy region. Therefore, the lowest charge transfer band due to excitation of an electron from metal t_{2g} level to unfilled molecular orbital derived from the π^* level of the ligands ($t_{2g} \rightarrow t_{1u}$ or t_{2u}) should appear comparatively in high energy region compared to those due to $t_{2g} \rightarrow e_g^*$ transitions.[8]

In the spectra of all the complexes four to five bands appear within 320-700 nm range. Two bands in the low energy region (500-700 nm) have very low values of the extinction coefficient (3-30). These very weak bands could be assigned to spin forbidden transitions ($^1A_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$). In the Nujol mull spectra, one moderately intense band around 400 nm, had a shoulder around 390 nm and another band appeared around 340 nm. In the spectra taken in chloroform solution only one band around 400 nm was present and no split has been observed. The bands at 400 and 340 nm have been assigned to spin allowed ($^1A_{1g} \rightarrow {}^1T_{1g},$ $^1T_{2g}$) transitions. The split in the 400 nm band may be either due to lowering the symmetry from O_h or due to vibrational structure of the $C\equiv O$ stretching mode which is around 2000 cm^{-1} for the ground state of the complexes. It will be difficult to set aside one reason for the other for the split of the band, however, the amount of splitting ($\simeq 2000$ cm^{-1}) does indicate that the split may be due to the vibrational coupling. These bands could have been due to charge transfer, but, in a d^6 system one should expect charge transfer bands to appear on a much high energy

Table VI.3

Electronic spectral data of the complexes

Complex	Chloroform solution λnm	ε	Nujol mull λnm	Assignment	10 Dq cm^{-1}	B cm^{-1}	C cm^{-1}	β	Second band $^1A_{1g} \to {}^3T_{2g}$ nm	Difference of splitting third band cm^{-1}
1	2	3	4	5	6	7	8	9	10	11
RuH(acac)(CO)(PPh$_3$)$_2$	–	–	585	$^1A_{1g} \longrightarrow {}^3T_{1g}$	27,168	350	3,358	0.54	503	2112
	–	–	–	$^1A_{1g} \longrightarrow {}^3T_{2g}$						
	420	2050	425) 390)	$^1A_{1g} \longrightarrow {}^1T_{1g}$						
	–	–	340	$^1A_{1g} \longrightarrow {}^1T_{2g}$						
RuH(dbm)(CO)(PPh$_3$)$_2$	605	4	580	$^1A_{1g} \longrightarrow {}^3T_{1g}$	28,320	314	3,930	0.48	525	1831
	–	–	–	$^1A_{1g} \longrightarrow {}^3T_{2g}$						
	410	2514	420) 390)	$^1A_{1g} \longrightarrow {}^1T_{1g}$						
	–	–	340	$^1A_{1g} \longrightarrow {}^1T_{2g}$						

Table VI.3 (contd.)

1	2	3	4	5	6	7	8	9	10	11
RuH(ba)(CO)(PPh$_3$)$_2$	590	3	590	$^1A_{1g} \longrightarrow {}^3T_{1g}$	28,110	314	3,720	0.48	514	2060
	500	29	-	$^1A_{1g} \longrightarrow {}^3T_{2g}$						
	410	2174	430) 395)	$^1A_{1g} \longrightarrow {}^1T_{1g}$						
	-	-	340	$^1A_{1g} \longrightarrow {}^1T_{2g}$						
RuCl(acac)(CO)(PPh$_3$)$_2$	605	3	580	$^1A_{1g} \longrightarrow {}^3T_{1g}$	29,709	256	4,393	0.40	538	1926
	510	6	515	$^1A_{1g} \longrightarrow {}^3T_{2g}$						
	395	2417	410) 380)	$^1A_{1g} \longrightarrow {}^1T_{1g}$						
	-	-	340	$^1A_{1g} \longrightarrow {}^1T_{2g}$						
RuCl(dbm)(CO)(PPh$_3$)$_2$	580	26	585	$^1A_{1g} \longrightarrow {}^3T_{1g}$	28,953	331	3,953	0.5	509	1832
	515	26	510	$^1A_{1g} \longrightarrow {}^3T_{2g}$						
	400	2500	420) 390)	$^1A_{1g} \longrightarrow {}^1T_{1g}$						
	-	-	330	$^1A_{1g} \longrightarrow {}^1T_{2g}$						

Table VI.3. (contd.)

1	2	3	4	5	6	7	8	9	10	11
RuCl(ba)(CO)(PPh$_3$)$_2$	600	3	580	$^1A_{1g} \longrightarrow {}^3T_{1g}$	26,551	332	3,295	0.5	517	1960
	510	3	–	$^1A_{1g} \longrightarrow {}^3T_{2g}$						
	430	2526	430) 395)	$^1A_{1g} \longrightarrow {}^1T_{1g}$						
	–	–	350	$^1A_{1g} \longrightarrow {}^1T_{2g}$						

level and hence, the assignments given in Table VI.3 are preferred. From the position of the bands, the values of 10Dq, B, C, β and the position of the band due to $^1A_{1g} \rightarrow ^3T_{2g}$ transition have been calculated. The values are within the acceptable range of those found in other octahedral ruthenium(II) complexes.

Thus, on the basis of the analytical data, magnetic and spectral (ir and visible) studies, the following three structures are possible for these complexes. However, without X-ray single crystal studies it is not possible to prefer one over the other:

$$(X = Cl \text{ or } H; \; R = C_6H_5/CH_3)$$
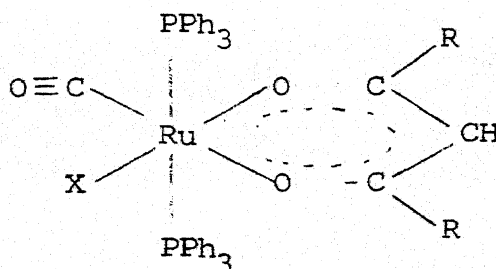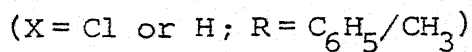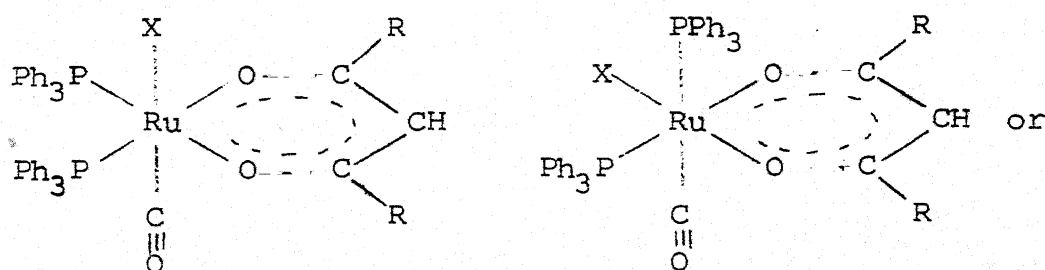
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3. N. Ahmad, J.J. Levison, S.D. Robinson, and M.F. Uttley, "Inorganic Syntheses", Vol. XV, Ed. G.W. Parshall, McGraw-Hill Co., New York, 1974, page 48.

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5. F.A. Cotton and G. Wilkinson," Advanced Inorganic Chemistry", A comprehensive Text, 3rd Edn., Interscience Publishers, New York, 1972, page 691-92.

6. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John-Wiley & Sons, Inc., New York, N.Y., 1964.

7. C.J. Ballhausen and H.B. Gray in "Coordination Chemistry", Vol. 1, Ed. A.E. Martell, Van Nostrand Reinhold Co., New York, page 52, 1971.

8. C.J. Ballhausen and H.B. Gray in "Coordination Chemistry", Vol. 1, Ed. A.E. Martell, Van Nostrand Reinhold Co., New York, page 60, 1971.

S U M M A R Y

Over the past two decades a large amount of work has
been done on the complexes of ruthenium with tertiary-phos-
phines and arsines. These complexes act as good catalysts in
various reactions. Besides these complexes have been used as
starting materials for the syntheses of many ruthenium(II)
and ruthenium(III) complexes. Present work concerns with the
reactions of some of the ruthenium(III) and ruthenium(II)
complexes of triphenylphosphine and triphenylarsine with a
number of other ligands. The structures of the complexes
formed as a result of these reactions have been investigated
using various physicochemical techniques.

The reactions of [RuCl$_3$(AsPh$_3$)$_3$] have been studied with
the ligands containing nitrogen, oxygen and sulphur donor atoms.
Four types of behaviours are exhibited by the complex.

(1) Displacement of one of the triphenylarsine molecules by one molecule of the ligand giving complexes of the type $[RuCl_3(AsPh_3)_2L]$ ($L = CH_3CH_2CH_2CN$, $CH_2=CHCN$, dmf, CH_3CHO, C_6H_5CHO, $C_2H_5NO_2$).

(2) Displacement of two triphenylarsine molecules by one molecule of a bidentate ligand giving $[RuCl_3(AsPh_3)L]$ ($L = bipy$, phen).

(3) Reduction of ruthenium(III) to ruthenium(II) with partial displacement of the triphenylarsine groups giving complexes of the type $[RuCl_2(AsPh_3)_2L_2]$ ($L = CH_3CN$, $CH_3CH_2CH_2CN$, $CH_2=CHCN$).

(4) The formation of ionic ruthenium(III) complexes of the types $M[RuCl_4(AsPh_3)_2]$ ($M = Me_4N^+$, Et_4N^+), $Ph_4As[RuCl_4(AsPh_3)_2]$. $2Me_2CO$ and $M[RuCl_3X(AsPh_3)_2]$ ($M = Me_4N^+$; $X = Br$, I) on reacting the complex with tetraalkyl-ammonium or tetraphenyl-arsonium halides.

On the basis of the electronic spectral and the chemical reactions studies an equilibrium between hexa- and penta-coordinated species has been postulated in a number of complexes.

The reactions of potassium/sodium thiocyanate, carboxylic acids with $[RuCl_3(AsPh_3)_3]$ have been studied. As a result of these reactions dimeric complexes $[Ru(SCN)_3(AsPh_3)_2]_2$ and $[RuCl_2(AsPh_3)_2(RCOO)]_2$ have been obtained. It has been shown that these have thiocyanato and chloro bridges respectively.

The reactions with ammonia, amine and hydrazine resulted in the following type of complex $[RuCl_2(AsPh_3)_2L_2]$ ($L = NH_3$, CH_3NH_2, NH_2NH_2, $C_6H_5NHNH_2$). A new ruthenium(III) complex $[RuBr_3(AsPh_3)_3]$ has been synthesized and studied. The electronic spectral studies indicate that there is an equilibrium between hexa- and penta-coordinated species in solution for $[RuBr_3(AsPh_3)_3]$ and $[RuCl_2(AsPh_3)_2(RCOO)]_2$ complexes.

Compounds of the type $[RuX_2(bdk)L_2]$ ($X = Cl$, Br; $bdk = \beta$-diketonate; $L = PPh_3$, $AsPh_3$) have been obtained when β-diketones were allowed to react with the ruthenium(III) phosphine and arsine complexes. A few of these complexes showed high value of magnetic moment than expected for the spin paired ruthenium(III) octahedral complexes. The high values of the magnetic moment have been explained by the presence of quartet or sextet spin state near the ground doublet spin state. The esr spectra of these complexes have also been studied. These studies indicate the octahedral geometry with tetragonal distortion. In one case the distortion is rhombic. The presence of quartet or sextet spin state has also been suggested by such studies in one of the complexes.

The reactions of β-diketones with polymeric and dimeric ruthenium(II) complexes viz., $[RuCl_2(PPh_3)_2]_n$ and $[RuCl_2(AsPh_3)_2]_2$ resulted in the formation of dimeric complexes of the type $[RuCl(bdk)L_2]_2$ ($bdk = \beta$-diketonate; $L = PPh_3$, $AsPh_3$) bridging

through chlorine atoms. Various physical methods have been used to understand their geometry. Further, the reactions of β -diketones with hydrido chloro carbonyl and dihydrido-carbonyl phosphine complexes of ruthenium(II), viz., $[RuH_2(CO)-(PPh_3)_3]$ and $[RuHCl(CO)(PPh_3)_3]$ gave monomeric complexes $[RuH(bdk)(CO)(PPh_3)_2]$ and $[RuCl(bdk)(CO)(PPh_3)_2]$ respectively.

The ruthenium(III) complex $[RuCl_3(AsPh_3)(OAsPh_3)_2]$ has been restudied. It is found that this complex should be formulated as $[RuCl_3(AsPh_3)_2(OAsPh_3)]$. The reactions of this complex with nitric oxide and carbon monoxide gases resulted in the formation of two new ruthenium(II) complexes $[RuCl_3(NO)-(AsPh_3)(OAsPh_3)]$ and $[RuCl_2(CO)_2(AsPh_3)(OAsPh_3)]$. Apart from this a new isomer of $[RuCl_3(AsPh_3)_3]$ has been synthesized and proved to be different from the brown isomer by the esr and magnetic studies. Various other physical methods have also been used to study these complexes.

LIST OF PUBLICATIONS

1. Ruthenium(III) and Ruthenium(II) Complexes containing Triphenylarsine and other Ligands,

    K. Natarajan, R.K. Poddar and U. Agarwala,
    J. Inorg. Nucl. Chem., 38, 249 (1976).

2. Mixed Complexes of Ruthenium(III) and Ruthenium(II) with Triphenylphosphine or Triphenylarsine and other Ligands,

    K. Natarajan, R.K. Poddar and U. Agarwala,
    J. Inorg. Nucl. Chem. (in press).

3. Some new β-Diketone Complexes of Ruthenium(III) with Triphenylphosphine and Triphenylarsine,

    K. Natarajan and U. Agarwala,
    Bull. Chem. Soc. Japan (in press). 10, 2877 (1976).

4. New Ruthenium(III) and Ruthenium(II) Complexes with Triphenylarsine and Triphenylarsine Oxide,

    K. Natarajan, R.K. Poddar and U. Agarwala,
    Inorg. Nucl. Chem. Lett. (in press). 12, 749 (1976).

5. Tetraphenyldiarsine Complex of Ruthenium(III) and its Reactions with various Ligands,

    A. Garg, K. Natarajan and U. Agarwala,
    J. Org. Met. Chem. (communicated).

6. β-Diketonato(triphenylphosphine)- and (triphenylarsine) Complexes of Ruthenium(III),

    K. Natarajan and U. Agarwala,
    Bull. Chem. Soc. Japan (communicated).

VITAE

K. Natarajan was born on 9th May, 1949 in Tirupur (Tamil Nadu). After passing the School Final Examination from Bishop Ubagarasamy High School, Tirupur, he joined the P.S.G. Arts College, Coimbatore in 1966, from where he did his Pre-University and B.Sc. Courses. Subsequently in 1970 he joined the Masters Programme in Analytical and Inorganic Chemistry at the A.C. College of Technology, University of Madras, Madras and obtained the M.Sc. degree in 1972. In July 1972 he joined the Ph.D. Programme in Chemistry at Indian Institute of Technology, Kanpur. At present he is a Research Assistant in the Department of Chemistry, Indian Institute of Technology, Kanpur.

ADDENDUM

The yields of the products were more than 80% in most of the cases except in the following:

Yield	page	Reaction
60%	28	(viii) & (ix)
40%	115	(a)(i)
70%	116	(a)(iii)
60%	134	(i),(ii) & (iii)
60%	135	(iv),(v) & (vi)

CHAPTER II

DISCUSSION

page 44
line 5   (i) It has been recently reported[1] that the complex $[Ir(CS_2)(CO)(PPh_3)_3]^+$ should be formulated as $[Ir(S_2CPPh_3)-(CO)(PPh_3)_2]^+$. It is, therefore possible that the complex $[RuCl_3(AsPh_3)_2(CS_2)]$ may not be a CS_2 complex and should be formulated as $[RuCl_3(AsPh_3)(S_2CAsPh_3)]$. However, on grinding with Nujol mull, a band at 920 nm appeared in the electronic spectra taken in Nujol mull. This indicated the presence of five coordinated species. The exact mode of bonding of CS_2 molecule in the complex can be determined only by X-ray crystallography.

    (ii) The statement on page 51 of the thesis that $[RuCl_3(AsPh_3)_2]$ has a square pyramidal structure in the solid state is deleted from the text of the thesis.

(1) G.R. Clark, T.J. Collins, S.M. James, W.R. Roper and K.G. Town, Chem. Comm., 475 (1976).
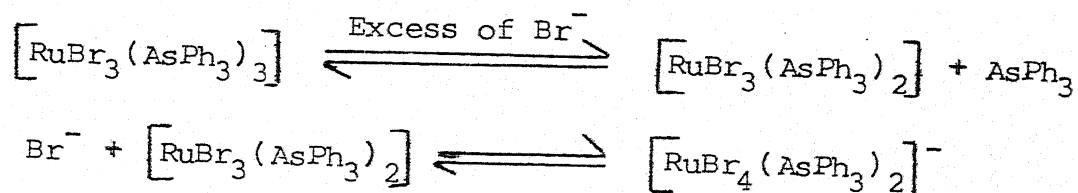
page 51
line 18   It will be very difficult to assign a reason for the

discrepancy in the band positions (910 nm^2 $\underline{vs}$ 776 nm^3) in the

low energy region of the visible spectrum of $\left[RuCl_3(AsPh_3)_2\right]$,

which might, however, be due to the difference in the nature

of the solvent in which the spectra were taken. In one case

benzene was used while in the other case chloroform. Such a

difference of about 40 nm was also observed in the case of

$\left[RuCl_3(AsPh_3)_2(CH_3CN)\right]$ in benzene (900 nm) and in chloroform

(860 nm).

CHAPTER III

EXPERIMENTAL

page 83   There is a possibility of the following equilibria to

exist in solution

$$\left[RuBr_3(AsPh_3)_3\right] \; \underset{\xrightarrow{\hspace{2cm}}}{\overset{Excess\ of\ Br^-}{\xleftarrow{\hspace{2cm}}}} \; \left[RuBr_3(AsPh_3)_2\right] + AsPh_3$$

$$Br^- + \left[RuBr_3(AsPh_3)_2\right] \; \underset{\xrightarrow{\hspace{1.5cm}}}{\xleftarrow{\hspace{1.5cm}}} \; \left[RuBr_4(AsPh_3)_2\right]^-$$

In order to comment on this equilibria, the following experi-
ments were performed.

   (i) Reactions of $\left[RuBr_3(AsPh_3)_3\right]$ with tetraalkylammonium

bromides were carried out similar to the ones described on page

27 (reaction vi). In all the cases the attempts to isolate

tetraalkylammonium salts of the species $\left[RuBr_4(AsPh_3)_2\right]^-$ have

failed.

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(2) Chapter II, page 51, line 17 of the thesis.

(3) P.T. Manoharan, P.K. Mehrotra, M.M. Taqui Khan and
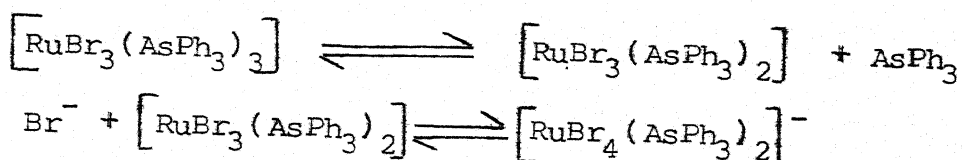   R.K. Andal, Inorg. Chem., $\underline{12}$, 2753 (1973).

(ii) The electronic spectrum of $\left[RuCl_3(AsPh_3)_3\right]$ was taken in chloroform solution ($\sim 10^{-3}M$) which showed a band at 910 nm. 1 ml of a saturated solution of lithium chloride in methanol was added to 10 ml of the above solution and the spectrum was recorded. In the spectrum the band at 910 nm disappeared and a new band appeared at 600 nm, besides a band at 520 nm.

(iii) The electronic spectrum of $\left[RuBr_3(AsPh_3)_3\right]$ ($\sim 10^{-3}M$) in nitrobenzene was recorded.

DISCUSSION

The dissociation behaviour of $\left[RuBr_3(AsPh_3)_3\right]$ given on page 77 of the thesis is further substantiated by the following experimental results.
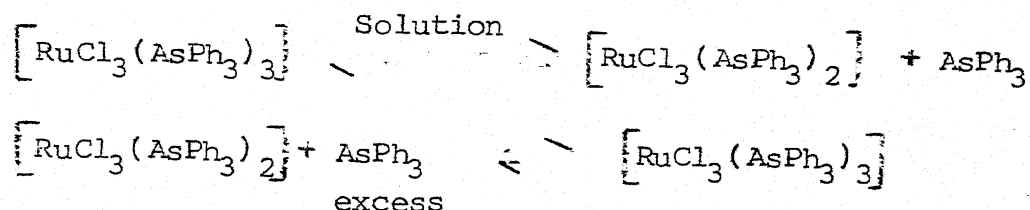
If the following equilibrium

$$\left[RuBr_3(AsPh_3)_3\right] \rightleftharpoons \left[RuBr_3(AsPh_3)_2\right] + AsPh_3$$

$$Br^- + \left[RuBr_3(AsPh_3)_2\right] \rightleftharpoons \left[RuBr_4(AsPh_3)_2\right]^-$$

is assumed, one should be able to isolate the tetraalkyl-ammonium salts of the species $\left[RuBr_4(AsPh_3)_2\right]^-$ similar to $\left[RuCl_4(AsPh_3)_2\right]^-$ by the addition of tetraalkylammonium bromides as obtained by T.A. Stephenson.[4,5] The failure to isolate such compounds suggested that $\left[RuBr_4(AsPh_3)_2\right]^-$ species did not form during the reaction in solution. It may however be $\left[RuBr_2(AsPh_3)_3\right]^+$ as suggested by the study of its electronic spectra in the

(4) T.A. Stephenson, Inorg. Nucl. Chem. Lett., 4, 687 (1968).
(5) T.A. Stephenson, J. Chem. Soc. (A), 889 (1970).

presence or absence of triphenylarsine (page 76 of the thesis).

The electronic spectrum of $[RuCl_3(AsPh_3)_3]$ taken in chloroform solution showed a band at 910 nm. This band disappeared if a solution of lithium chloride in methanol was added to the solution of $[RuCl_3(AsPh_3)_3]$ and a new band appeared at 600 nm besides a band at 520 nm. This suggested the presence of hexacoordinated $[RuCl_4(AsPh_3)_2]^-$ species which was further supported by the separation of compounds $R_4N[RuCl_4(AsPh_3)_2]$ (R = Me or Et) on the addition of the corresponding tetraalkyl-ammonium chloride and then stirring it for several hours. Also, the band at 910 nm disappeared from the spectrum of $[RuCl_3(AsPh_3)_3]$ on the addition of triphenylarsine indicating the dissociation of triphenylarsine from $[RuCl_3(AsPh_3)_3]$ in solution.

$$[RuCl_3(AsPh_3)_3] \xrightarrow{\text{Solution}} [RuCl_3(AsPh_3)_2] + AsPh_3$$

$$[RuCl_3(AsPh_3)_2] + \underset{\text{excess}}{AsPh_3} \longleftarrow [RuCl_3(AsPh_3)_3]$$

The conductivity of $[RuBr_3(AsPh_3)_3]$ can also be explained by assuming the following self-ionization:

$$2[RuBr_3(AsPh_3)_2(C_6H_5NO_2)] \rightleftharpoons [RuBr_4(AsPh_3)_2]^-$$
$$+ [RuBr_2(AsPh_3)_2(C_6H_5NO_2)]^+.$$
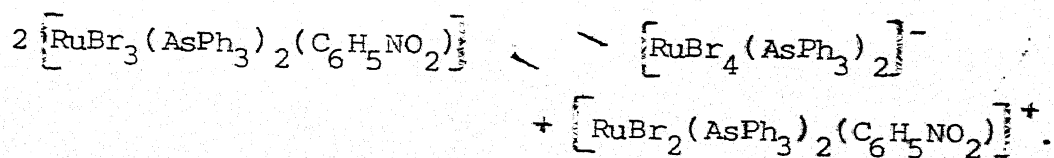
This possibility is ruled out on the following grounds:

The electronic spectrum of $[RuBr_3(AsPh_3)_3]$ in nitrobenzene solution showed a band at 970 nm indicating the presence of penta-coordinated species but no band appeared in the 600 nm region. This suggested the absence of hexacoordinated species like $[RuBr_4(AsPh_3)_2]^-$. Since in the self-ionization process both penta- and hexacoordinated species were indicated, the absence of the band around 600 nm suggested that the presence of hexa-coordinated species does not exist in solution and thereby the absence of the self-ionization.

CHAPTER IV

DISCUSSION

page 102
line 18   An alternative explanation which could explain the magnetic susceptibility data could be as follows:

Magnetic Data: The values of the magnetic moments of Ru(III) complexes as pointed out in Chapter IV, should not exceed 2.3 BM (15). Thus, all the β-diketone complexes except no. 1, 2, 5, and 6 (Table IV.1) show normal values suggesting the presence of Ru(III) in the complexes. The higher values in four complexes could have been due to the presence of some impurity of Ru(IV) complex formed during the course of the reaction and which possibly could not be separated by recrystallization process. Thus, the larger the percentage of impurity of Ru(IV) complex, the higher will be the value of the magnetic moments. It will not be out of place to indicate here that $RuCl_3 \cdot xH_2O$ used for the

preparation of the starting materials, $\left[RuX_3(AsPh_3)_3\right]$, $\left[RuCl_3(PPh_3)_3\right]$ and $\left[RuBr_3(PPh_3)_2 \cdot MeOH\right]$, was treated to remove any impurities due to Ru(IV) according to the methods described in the literature.[6,7]

The nmr spectra of some of these complexes taken in $CDCl_3$ did not show the presence of a number of isomers.

Electron Spin Resonance Spectral Data: The maximum symmetry of all the complexes can not be more than C_{2v} if only the nearest atoms around Ru(III) are taken into consideration. In that case, one should expect three values of 'g' (one each along the three principal axes) in spectrum of every complex. Thus, the spectrum of $\left[RuCl_2(ba)(PPh_3)_2\right]$ exhibits three bands with $g_1 = 2.34$, $g_2 = 1.93$, and $g_3 = 1.83$. In the spectra of all the remaining complexes except $\left[RuCl_2(dbm)(PPh_3)_2\right]$ and $\left[RuBr_2(dbm)-(AsPh_3)_2\right]$, only two bands appeared. The presence of two bands in the spectra of these complexes may be due to a change in symmetry of the field from the lower to the higher one as discussed earlier. However, it is also possible that only two 'g' values for these complexes may be arising because of the fortuitously similar values of the two of the three 'g' values expected.

The spectra of $\left[RuCl_2(dbm)(PPh_3)_2\right]$ and $\left[RuBr_2(dbm)(AsPh_3)_2\right]$ showed five to six bands. In these cases, a mixture of isomers

(6) F.A. Cotton and G. Wilkinson, Adv. Inorg. Chem., 2nd Edn., Wiley Eastern Pvt. Ltd., New Delhi, 1969, p. 998.
(7) B.R. James and R.S. McMillan, Inorg. Nucl. Chem. Lett., 11, 837 (1975).

with different sets of 'g' values could be present and each
isomer will show its set of two or three 'g' values, thus result-
ing in the appearance of five to six bands.

The above explanations for the esr spectra and the magne-
tic moment data are only tentative.

Electronic Spectra: In order to explain the electronic spectra
of these complexes, it has been tacitly assumed on the basis of
"Average Environment Rule" that the symmetry of the ligand field
around metal ion is pseudo-octahedral. Any departure from O_h
symmetry will either split or deform the bands arising due to
d-d transitions. In the spectra of these complexes the shape
of the band assigned to d-d transition was found to be unsymme-
trical.

CHAPTER V

EXPERIMENTAL

128   (i) The reactions of $\left[RuCl_3(AsPh_3)_2(OAsPh_3)\right]$ with ligands
such as acetonitrile, butyronitrile, dmf and dmso were carried
out under similar conditions described in the thesis (Chapter II,
page 25 reaction (i)) except that nitrogen instead of oxygen
atmosphere was maintained. These reactions resulted in the
formation of the same complexes, $\left[RuCl_3(AsPh_3)_2L\right]$ (L = CH_3CN,
$CH_3CH_2CH_2CN$, dmf, dmso) and no oxygen evolution was detected.
After separating the compounds, triphenylarsine oxide was
obtained from the mother liquor in 80-90% yield.

(ii) $[RuCl_3(AsPh_3)_3]$ (0.22 g, 0.2 mmole) was taken in benzene (10 ml) and triphenylarsine oxide (0.096 g, 0.3 mmole) in 5 ml of warm benzene was added. The solution was heated under reflux for 3 hr under nitrogen atmosphere and cooled. The resulting solution was concentrated under nitrogen atmosphere whereby a reddish-brown compound was obtained. It was centrifuged, washed with benzene and ether and dried under vacuum; yield 40%. Analyses: Calculated for $[RuCl_3(AsPh_3)_2(OAsPh_3)]$: C, 56.77; H, 3.94; Cl, 9.32. Found: C, 56.41; H, 3.85; Cl, 9.82; melting point, $218^{\circ}C$; the infrared spectra was exactly the same as that for $[RuCl_3(AsPh_3)_2(OAsPh_3)]$.

DISCUSSION

(i) In the reformulation of $[RuCl_3(AsPh_3)(OAsPh_3)_2]$ as $[RuCl_3(AsPh_3)_2(OAsPh_3)]$ the possibility of this being a dioxygen complex or more likely starting material contaminated by a dioxygen complex is not possible for the following reasons.

(a) The analytical data fit well with the formula $[RuCl_3(AsPh_3)_2(OAsPh_3)]$ or with $[RuCl_3(O_2)(AsPh_3)_3]$. But the possibility of the latter complex can be ruled out on the basis of its being unstable[8] and non-preferential geometry (7 or 8 coordination) of ruthenium. Our complex is very stable one having a sharp melting point.

(8) B.R. James, L.D. Markham, A.D. Rattray and D.K.W. Wang, Inorg. Chim. Acta, 20, L25 (1976).

(b) The reactions of this complex with ligands such as acetonitrile, butyronitrile, dmf and dmso resulted in the complexes $[RuCl_3(AsPh_3)_2L]$. Besides, triphenylarsine oxide was also obtained from the mother liquor in 80-90% yield and no oxygen was evolved.

(c) A reaction of $[RuCl_3(AsPh_3)_3]$ with triphenylarsine oxide under nitrogen atmosphere yielded the complex $[RuCl_3(AsPh_3)_2 (OAsPh_3)]$ in 40% yield. This compound has been compared (analytical data, melting point and infrared) with the one reported by us and seems to be identical.

(ii) The 'g' values obtained from the esr spectra of the complexes which have been reported to four decimal places are now mentioned only to two decimal places.

(iii) In the preparation of $[RuCl_3(AsPh_3)_2]$ from $[RuCl_3(AsPh_3)_2.MeOH]$ (page 116) about one molar triphenylarsine was added which is not at all necessary. The experiment in the thesis was carried out with an intension of preparing $[RuCl_3(AsPh_3)_3]$; but it was observed that with equimolar addition of triphenylarsine, $[RuCl_3(AsPh_3)_3]$ (pink isomer) was not obtained as the major product. Instead, $[RuCl_3(AsPh_3)_2]$ was obtained in about 70% yield and a minor product (not mentioned in the thesis) obtained was $[RuCl_3(AsPh_3)_3]$ (pink) in about 10% yield. The minor product was obtained only after cooling the mother liquor to $0^{\circ}C$ for a few hours. When about four molar excess of triphenylarsine was used (page 115, reaction (i)) the pink compound was obtained in about 40% yield.

CHAPTER VI

DISCUSSION

For the complexes $\left[RuX(\beta\text{-diketonate})(CO)(PPh_3)_2 \right]$ (X = H

or Cl), three possible structure are proposed (page 144). The

fourth structure given below is also possible.
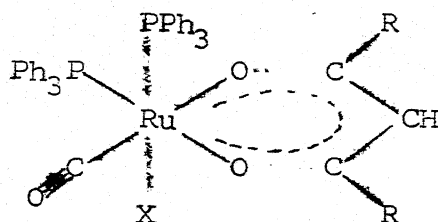
Also, in the case of unsymmetrical β-diketone (benzoylace-

tone) complexes there are seven possible isomers.

The suggestions concerning above points by the reviewers

are gratefully acknowledged.